BLEACH-PLANT CAPITAL REDUCTION WITH RAPID D_0 BLEACHING AND SIMPLIFIED (D/E/D) STAGES

Project 4201
(DOE DE-FC07-971D13562)

Final Report

to

U.S. DEPARTMENT OF ENERGY

August 2000

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

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By

T.J. McDonough, C.E. Courchene, and J.-C. Baromès

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Summary

The objective of this work was to demonstrate the capabilities of a bleaching sequence that combined a short retention time initial chlorine dioxide stage, referred to as rapid D_0, (D_0^R), with simplified bleaching stages, (D_1/E/D_2), that required only one final bleach washer. The test sequence D^R(EPO)(D/E/D) was compared to a control sequence, D(EPO)D, for both hardwood and softwood pulps.

The capabilities of the D^R(EPO)(D/E/D) sequence were successfully demonstrated. An existing three- or four-stage bleach plant can be converted to the more powerful D^R(EPO)(D/E/D) sequence without the major capital cost of additional washers. The results from this study showed that the D^R(EPO)(D/E/D) sequence can reach 85 brightness on SW with 2.8% total ClO_2, while the control sequence, D(EPO)D, required 3.9% ClO_2. There was a corresponding decrease in AOX for the test sequence. The strength of pulp bleached in the test sequence was similar to or slightly higher than the control. For the HW pulp, the test sequence reached 88 brightness with 2.2% ClO_2, compared to 3.3% ClO_2 for the control. There was a corresponding decrease in AOX generation with the lower chemical requirements. The final viscosity and pulp strength for the test sequence on HW was significantly higher than the corresponding values for the control sequence.

IPST matching funds were used to test the feasibility of the D_0^R stage by some limited mill trials on SW pulp. Samples were collected immediately downstream of a mill ClO_2 mixer and the residual chemical was determined after a series of retention times ranging from 20 seconds to 5 minutes. This time was controlled by holding each sample then adding sodium sulfite to destroy the residual ClO_2 and stop the reaction. The samples were then subjected to a standard caustic extraction stage in the laboratory. The extracted kappa number was compared to the kappa number following the mill's full retention time D_0 and (EO) stages. At a kappa factor (KF) of 0.16, the delignification after a D_0 time of only 29 seconds was 87% of what the mill was reaching in their D(EO) stages, and after a 5-minute D_0 stage, 98% delignification was possible. After 29 seconds, 83% of the applied ClO_2 was consumed, while 94% was consumed after 5 minutes.

Additional tests were conducted in the lab using D^RE stages on SW and HW pulps from the same mill as the trials. A KF of 0.16 was used for the SW and 0.23 for the HW. For the SW, 89% of the ClO_2 was consumed in 120 seconds, while for HW, 68% was consumed. The E-stage kappa number of 10.5 for the SW was higher than the 8.4 reached in the mill trials at a similar D_0 retention time. The E stage kappa number for the HW was 6.9 after 120 seconds in the D_0 stage. Comparison of the lab bleaching to the mill trials showed that mixing in the mill appeared to be more efficient. It also served to demonstrate that any tests done in the lab could be duplicated or even exceeded by the full-scale process.

Kraft pulps were prepared in the lab from both loblolly pine (SW) and sweetgum (HW) chips for comparison of the D^R(EPO)(D/E/D) and D(EPO)D sequences. The kappa numbers of the SW and HW were 29.1 and 15.6, respectively. A later batch of SW pulp from the same chips used for some of the testing had a kappa number of 25.8.

Initial trials of D^RE stages on these lab pulps were done at a KF of 0.10, a D_0 temperature of 45°C, and a consistency of 3.3%. For the SW, the consumption of the applied ClO_2 was 94% after 30 seconds and 97% after 120 seconds. The E-stage kappa number was 13.2 after the 30-second D stage and 12.7 after the 120-second stage. For the HW, the ClO_2 consumption went from 81% at 30 seconds to 88% after 120 seconds. The respective E-stage kappa numbers were 8.9 and 8.4. The rapid D_0 stage was very efficient at the low KF, but the extracted kappa numbers were too high for a full sequence to reach high brightness without excessive chemical consumption.

Subsequent testing with the D_0^R stage was done at a higher KF (0.15) and a higher temperature (70°C). In addition, the (EO) stage was replaced with an (EPO) stage with 0.8% H_2O_2. On SW, 99% of the applied ClO_2 was consumed in 60 seconds, while 94% was consumed by the HW. After a 60-second D_0 stage, the (EPO) kappa number was 6.6 for the SW and 6.1 for the HW. Only slight reductions in kappa number, to 6.3 for SW and 5.9 for HW, were achieved by extending the D_0 time to 240 seconds.

These D^R stages were stopped by quenching with Na_2SO_3, to achieve a precise retention time. Tests were then conducted with D^R(EPO) stages in which the D stage was quenched with NaOH instead. With NaOH quenching, the (EPO) kappa number after the 60-second D_0 stage was somewhat lower, 5.9 for SW and 5.8 for HW. When 10% D_0 filtrate carryover was used in the (EPO) stage to simulate washer inefficiency, the (EPO) kappa number for the SW was 6.4 while for HW it was 5.9.

Optimization of the ($D_1/E_2/D_2$) stages was done with D^R(EPO) pulp made with 0.15 KF and 60 seconds in the D^R stage. The retention times were 8 minutes for D_1 and 4 minutes for E_2. The D_2 stage was ended when the ClO_2 residual was exhausted, up to a maximum of 180 minutes. The consistency was 10% and the temperature was 80°C for all three stages. Under these conditions, a brightness of 85 was reached with the pine pulp with a total of 3.58% ClO_2 applied, while a maximum brightness of 87.7 was reached with 4.58% ClO_2. The HW reached a brightness of 89 with 2.11% ClO_2 and 91 with 3.36% ClO_2.

The D_1 time was increased to 60 minutes and additional tests were done with the HW pulp at 80°C. The brightness values were 1-2 points lower than the 8-minute D_1 stages at an equivalent ClO_2 applied. There was no D_1 residual at 60 minutes, and it was evident that some reversion was occurring. Additional tests were done with lower temperatures in the D_1 stage at 60 minutes. At 70°C and 60 minutes for D_1, there was still a trace of residual ClO_2 and no evidence of reversion.

Fully bleached pulps were prepared with the D^R(EPO)(D/E/D) and D(EPO)D sequences for strength and filtrate testing. The target brightnesses of 85 for SW and 88 for HW were closely approached. The KF was 0.15 and the D^R time was 1 minute, while the time for the control D_0 stage was 30 minutes. Pulps using both 8-minute, 80°C and 60-minute, 70°C D_1 stages were used for the test sequence. For the SW, 3.9% ClO_2 was required for the test sequence with an 8-minute D_1 and 2.8% was required with the 60-minute D_1. The control sequence required 3.9% ClO_2 to reach the target brightness. The test sequence on the HW pulp (kappa number 15.2) required 2.1% and 2.2% ClO_2 for the 8 minute- and 60-minute D_1 stages, respectively. The control sequence required 3.3% ClO_2 to reach the 88 target brightness.

The SW control pulp had a final viscosity of 11.2, while the viscosities were 15.4 and 12.4 for the test sequences with 8-minute and 60-minute D_1 stages, respectively. The control sequence for the HW gave a viscosity of 9.6, while the test sequences had significantly higher viscosities, 16.7 and 15.4.

The test sequences applied to SW gave pulp with slightly higher tensile and burst strengths and similar tear strength, as compared to the control. The test sequences applied to HW resulted in 10-18% higher tensile, burst, and tear strengths than the control at 400 CSF. The test sequences had significantly higher tear strength at a given tensile strength.

The AOX results for the combined filtrates from the test sequences on SW were 0.73 kg/ADMT with the 8-minute D_1 with 3.9% total ClO_2 and 0.55 kg/ADMT for the 60-minute D_1 with 2.8% total ClO_2. The SW control with 3.9% ClO_2 had a combined AOX of 0.69 kg/ADMT. The HW test sequences generated combined filtrate AOX values of 0.39 and 0.42 kg/ADMT with 2.1 and 2.2% total ClO_2. The HW control generated a combined filtrate AOX of 0.61 kg/ADMT.

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Introduction

The adoption of elemental chlorine free (ECF) bleaching as a means of compliance with EPA's Cluster Rules has led many mills to plan for bleach plant reconfigurations that will continue to meet product quality and simultaneously reduce the discharge of chlorinated organic compounds (as determined by AOX). In many cases, these bleach plant reconfigurations are costly because they require additional capital equipment such as towers and washers. The industry will welcome any easily adapted and proven bleaching technologies that enable ECF bleaching to obtain high brightness with low AOX generation, while using existing equipment or minimizing the installation of new equipment.

One technology that could result in both capital equipment savings and AOX reductions is the use of a short retention time in the initial chlorine dioxide stage (D_0). Kinetic studies of different bleaching stages have shown that the reaction types are similar: a fast, initial reaction accounts for a majority of the bleaching effect, while a much slower second phase reaction produces the remainder of the bleaching effect.[1] A study of the kinetics of a D_0 stage has confirmed the existence of a very rapid initial delignification phase.[2] The temperature and pH were also shown to have a significant effect on the reaction rate.

Studies at IPST have shown that a "Rapid D_0" stage of one minute retention, with a 0.25 kappa factor, achieved 84% of the delignification of a 30-minute stage while generating only 42% of the AOX.[3,4] Characterization of the AOX generated at one minute showed it was more likely to be innocuous than the AOX produced under conventional conditions. The impact on delignification of decreasing the reaction time is smaller at lower kappa factors, allowing very rapid D_0 stages to be employed with little or no penalty in low kappa factor bleaching. When a Rapid D_0 stage is employed, the kappa factor can be reduced from 0.25 to 0.1 without significant brightness penalty by adding peroxide to the extraction stage. Combined effluent data indicate a 30% reduction in AOX and a 20% reduction in chlorine-to-carbon ratio when the D_0-stage reaction time is decreased from 30 minutes to 1 minute at 0.1 kappa factor.

A related study examined the effect of pH in the D_0 stage on the degree of delignification and the formation of AOX.[5] An initial pH of 4 was found to result in a lower extracted

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[1] Axegard, P., Moldenius, S., and Olm, L., "Basic Chemical Kinetic Equations Are Useful for an Understanding of Pulping Processes," *Svensk. Papperstid.* 82(5), 131 (1979)

[2] Germgard, U. and Teder, A., "Kinetics of Chlorine Dioxide Prebleaching," *Transactions of the CPPA Technical Section* 6(2), TR31 (1980)

[3] Schwantes, T.A. and McDonough, T.J., "The Effect of D Stage Reaction Time on the Characteristics of Whole Effluents and Effluent Fractions from D(EO) Bleaching of Oxygen Delignified Softwood Kraft Pulp," *1994 International Pulp Bleaching Conference,* 217-240, June 16, 1994, Vancouver, B.C.

[4] McDonough, T.J., "Rapid, Low-Impact ECF Delignification," *Annual Research Review Chemical Pulping and Bleaching*, Institute of Paper Science and Technology, Atlanta GA, 43-47, (March 22, 1995)

[5] Schwantes, T., McDonough, T., Malcolm, E., and Sonnenberg, L., "The Effect of D Stage pH on Effluent Quality: Characterization of Effluent Fractions from OD(EO) Bleaching of Softwood Kraft Pulp," *J. Pulp and Paper Science,* 22(6), J192-J197, (June 1996)

kappa number than an initial pH of 2. Fractionation and characterization of the effluents showed that at pH 4, the chlorine-to-carbon ratios (which may predict environmental effects) were lower than those at pH 2.

For a Rapid D_0 stage, the initial pH can be used together with temperature and ClO_2 concentration as control parameters to optimize the results for delignification and AOX formation. A Rapid D_0 stage would be accomplished by using a high-shear mixer followed by a short retention tube. The existing C or D_0 tower would then be available for use elsewhere in the bleaching sequence, allowing the power of the sequence to be significantly increased.

For subsequent ClO_2 bleaching stages, another technology, referred to as "Simplified Bleaching," has been developed by Histed to add a D stage with little capital investment, no additional washing stages being required.[6] This simplified scheme uses a short retention (8-minute) D_1 stage followed by a short (minute) E stage with no washing between the stages. This is followed by a conventional D_2 stage with no washing between the E and D_2 stages. The simplified (D/E/D) scheme was shown on a mill scale to produce fully bleached pulp with superior strength compared to a more conventional sequence.[7] The use of (D/E/D) bleaching together with other bleaching technologies and proper recycling of effluents through the bleach plant has been proposed as a means of retrofitting a five-stage bleach plant with minimum capital cost to provide ECF fully bleached pulp at good strength with low AOX discharge.[8]

The work proposed by IPST and reported here demonstrates the applicability of a bleach sequence using both a rapid D_0 stage and (D/E/D) stages for fully bleached pulps.

Objectives

The objectives of this research were to demonstrate the capability of the D_0^R(EOP)(D/E/D) sequence to bleach a hardwood (HW) kraft pulp to 89 brightness and a softwood (SW) kraft pulp to 85 brightness with acceptable strength and low AOX, and to identify optimal operating conditions for the process.

Four phases of work were planned. In the first, mill trials were conducted on SW followed by additional laboratory testing of mill SW and HW pulps. In the second, the Rapid D_0 (D_0^R) stage was optimized with respect to retention time and kappa factor on kraft pulps prepared in our laboratory from both softwood and hardwood. The third phase involved further bleaching with the simplified (D/E/D) scheme, while in the fourth, fully bleached pulps were produced under optimal conditions for evaluating strength and AOX discharge.

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[6] Histed, J.A. "Simplified Bleaching Process," *U.S. Patent #4,238,281*, Dec. 9, 1980

[7] Vega Canovas, R., Histed, J., Dontigny, D., and Vincent, P., "Simplified Bleaching at the LaTuque Mill," *Pulp & Paper Mag. Canada,* 93:4, T94-T96, (April 1992)

[8] Histed, J., "Reconfiguration of a Five-Stage Bleach Plant for Ultra-Low AOX Discharge," *1996 International Pulp Bleaching Conference,* 585-588, (1996)

Benefits to the Industry

The U.S. pulp and paper industry is undergoing a major transformation of its bleaching processes from those that depend on the use of chlorine and hypochlorite to those that will comply with effluent and emissions guidelines. According to 1993 data reported by Vice *et al.*,[9] of 85 U.S. bleach plants surveyed, eight employed the CEH sequence and 41 employed the (C+D)EHD sequence. In most cases, it is likely that the new limitations will require conversion to sequences based on the use of chlorine dioxide, oxygen, and peroxide to displace all, or nearly all, of the chlorine and hypochlorite presently used. It is unlikely, however, that simply substituting the new oxidants will be feasible with existing equipment.

As an example, the (C+D)EHD sequence may be cited. At first glance it seems possible to convert this bleach plant to a DEDP sequence with relatively minor equipment modifications. However, this latter sequence is less powerful and at many mills would be incapable of meeting pulp quality requirements unless the ClO_2 charges were so high as to be uneconomical and/or out of compliance with the new AOX limitations. The mill would then be faced with adopting alternatives such as the D(EOP)DED sequence, which will meet both quality and AOX requirements. The cost of this conversion would be substantial, perhaps $12 million (not including the cost of additional ClO_2 generation capacity), largely due to the requirement for a new ClO_2 mixer, tower, and washer. Conversion of an existing CEH sequence would also require a new ClO_2 stage.

The D_0^R(EOP)(D/E/D) sequence would provide a low-capital solution to this dilemma. In the case of a CEHD sequence, the D_0^R stage would be added with an efficient mixer and short retention tube ahead of the C-stage washer. The E stage would be converted to (EOP) while the H stage would become the D_1 stage. Another mixer and upflow tube would be added as an E stage between the D_1 and D_2 stages. No additional washers would be needed. This is significant because the washer is the most costly element of a conventional bleaching stage.

[9] Vice, K.M., Sieber, R.E., and Bicknell, B., "Costs of Upgrading Bleach Plants to Minimize COD Discharges," Paper 3-4, *1995 Nonchlorine Bleaching Conference Proceedings,* Miller Freeman.

Experimental

General Approach

The first testing to demonstrate the feasibility of the Rapid $D_0(D_0^R)$ stage was done in limited mill trials on SW, followed by laboratory trials of D_0^R stages applied to SW and HW pulps from the same mill.

Following the mill trials, kraft pulps were produced at IPST from both a hardwood and softwood species for all testing. Initial bleaching trials were done with D_0^RE partial sequences at a low kappa factor and varied retention times up to two minutes. Further testing was then done with a D_0^R(EPO) partial sequence at higher kappa factors. Two sets of trials were done under each condition, one to measure the residual chemical at each retention time and the second with quenching of the reaction at the end of the retention time with Na_2SO_3 and using the quenched pulp for the following extraction stage. Extracted kappa numbers were determined and used as a measure of the efficiency of the partial sequences.

Further testing of the D_0^R(EPO) partial sequence was done under the same conditions, with the exception that NaOH was used as a quenching agent instead of Na_2SO_3. The (EPO) pulps were then subjected to (D/E/D) bleaching trials in which the amounts of ClO_2 added in D_1 and D_2 were varied. The final brightnesses were compared to those obtained by a control sequence, D(EPO)D, as a function of total ClO_2 applied. Another set of (D/E/D) bleaching trials was done with increased D_1 time and varied temperatures. For the optimization trials, all stages were done in duplicate.

Optimum conditions were then chosen to produce a target brightness of 85 for SW and 89 for HW with both the D_0^R(EPO)(D/E/D) and D(EPO)D sequences for comparison of strength and effluent characteristics. Larger batches of pulp were made by running replicate bleaches and combining the resulting pulps.

Mill Trials

Trials were done in a mill in two periods on consecutive days with softwood pulp. Samples were collected from a sampling valve immediately downstream of the high-shear mixture for the D_0 stage. Samples were collected in 4-L plastic bottles and then held for specified retention times up to 5 minutes. At the end of the desired reaction time, samples in one set were added to potassium iodide (KI) solution and the residual ClO_2 was determined by titration with thiosulfate. Samples in another set, for a subsequent E stage, were quenched after the desired reaction time by adding Na_2SO_3. The quenched samples were then subjected to an extraction stage with 2.17% NaOH at 10% consistency for 60 minutes in sealed plastic bags in a water bath at 70°C. The kappa number and pH following the E stage were determined.

Pulping

Both sweetgum (*Liquidambar styraciflua)* and loblolly pine (*Pinus taeda*) logs were obtained from commercial sources and chipped in a 4' Carthage chipper at IPST. The chips were screened on a Williams screen, and the -1" to $+^1/_4$" fractions were retained for pulping. The chips were cooked in a batch digester with liquor circulation and external heating. The cooking conditions were 18.3% active alkali, 25% sulfidity, 4:1

liquor:wood ratio, and 170°C cooking temperature. The final H-factor was about 520 for the sweetgum and 1640 for the pine. The pulp was screened on a 12x43" Sprout-Waldron flat screen with 0.010" slots. The screened pulp was thickened to approximately 35% consistency and stored in a cold room at 4°C. The kappa number was determined on the screen accept pulp according to TAPPI T236.

Bleaching

Initial ClO_2 (D_0) stages were done in either a 20-L rapid-cycle reactor or a 2.1-L laboratory high-shear mixer. For bleach runs conducted to measure the residual and pH, a filtrate sample was withdrawn with a syringe from the reactor at the retention time and tested for pH and residual chlorine dioxide. Bleach runs to prepare pulp for additional testing were done by quickly injecting a quench solution of either sodium sulfite (Na_2SO_3) or sodium hydroxide (NaOH) to stop the reaction. The amount of Na_2SO_3 to add was calculated as twice the amount of chemical necessary to react with the corresponding ClO_2 residual for that retention time. The amount of NaOH added was that needed to raise the pH into the 8-10 range.

Later ClO_2 (D_1 and D_2) stages were done in sealed plastic bags in a temperature-controlled water bath. For the (D_1/E/D_2) stages, there was no washing after D_1, though a filtrate sample was collected to measure residual and pH, and a pulp sample was collected for brightness measurement. For the E stage, NaOH was added to the D_1 pulp to an initial pH of 11. After 4 minutes at 80°C, the E-stage pulp was acidified with sulfuric acid (H_2SO_4) and the required amount of ClO_2 was added, with no prior washing of the E-stage pulp. The D_2 stage was terminated when the color of the pulp indicated that nearly all of the ClO_2 had reacted, or after 180 minutes, whichever came first. The D_2-stage pulp was well washed and the brightness measured.

Simple extraction (E) stages were done in sealed plastic bags in a temperature-controlled water bath. Peroxide and oxygen reinforced extraction (EPO) stages were done in a pressurized peg mixer with electric heating. Oxygen was added as a gas to an initial pressure of 60 psig then slowly relieved to 0 psig in 30 minutes to simulate an upflow bleaching tower. For some runs, 10% of the total filtrate from the D_0 stage was added back to the pulp for the (EPO) stage to simulate mill bleach washer inefficiency.

AOX Testing

Filtrates were saved from each stage of the bleaching sequences to produce pulp for strength testing. A combined filtrate from the entire sequence was prepared by mixing the filtrates in the proportions determined by the stage consistency and carryover amount. The combined filtrate was acidified with HNO_3 to a pH of 2. Filtrates from the combined D(EPO) stages and the (D/E/D) stages of the D^R(EPO)(D/E/D) sequence were also tested separately. The AOX testing was done by Savannah Laboratories, Mobile, AL, according to EPA 1650.

Pulp Testing

The following procedures were used for pulp testing.

Testing	**Procedure**
Pulp viscosity	TAPPI T230
Brightness sheets	TAPPI T272
Brightness measurement (diffuse)	TAPPI T525
Brightness reversion	1-hr. forced air oven 105°C
Pulp refining (PFI mill)	TAPPI T248
Pulp freeness	TAPPI T227
Strength handsheets	TAPPI T205
Handsheet strength	TAPPI T220
Dirt	TAPPI T213

Results

Mill Trials

In January 1998, the feasibility of a rapid D_0 stage was tested in a bleached kraft mill of a member company as part of the industry matching effort. The bleach plant set-up allowed for collecting samples of pulp immediately downstream of the first-stage chlorine dioxide (D_o) mixer. The collected samples were quenched to stop the reaction at different times. Samples representing retention times from 26 to 300 seconds were collected in this manner. Additional samples were also collected but not quenched. These samples were tested for residual chlorine dioxide. The quenched D_0 samples were then subjected to a standard extraction (E) stage in the lab, and the E-stage kappa number was measured. Samples of the pulp following the mill's standard extraction stage (EO) were also collected and the kappa number measured for comparison. The details of the testing are shown in Appendix A. The kappa number after extraction is shown as a function of time in Figure 1, and the residual ClO_2 is shown in Figure 2. The results showed that with only 26 seconds of retention time, 87% of the delignification that the mill was achieving with their standard D_0(EO) stages was reached. In 300 seconds, 98% of the delignification was possible.

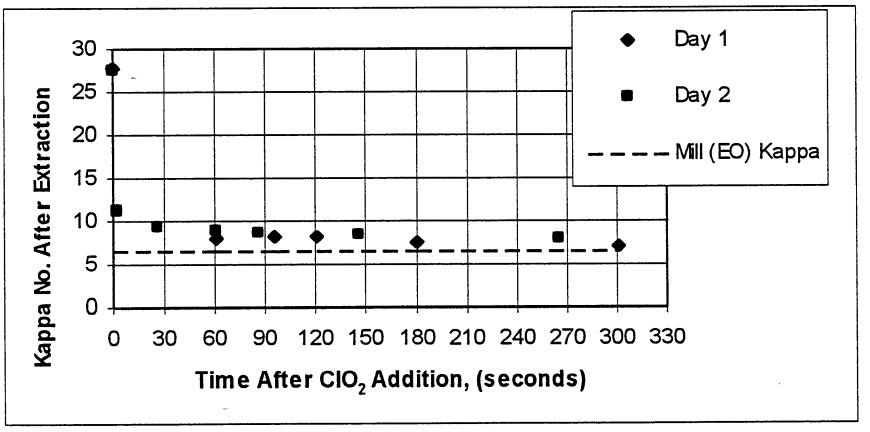

Figure 1. Kappa number vs. Retention Time for Mill Trials of SW Pulp

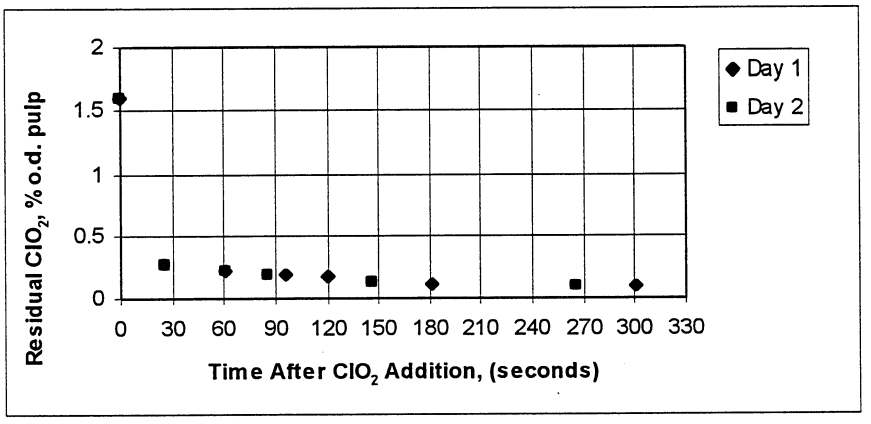

Figure 2. Residual ClO_2 vs. Retention Time for Mill Trials of SW Pulp

Lab Trials with Mill Pulps

Further experiments were done in the lab with a rapid D_0 stage on mill hardwood (HW) and softwood (SW) pulps from the same location as the mill trials. Initial testing was done in a rapid-cycle laboratory reactor. These results proved to be inconsistent so all testing was switched to a high-shear laboratory (CRS) mixer. For these tests, retention times of 30, 60, and 120 seconds were used. All other conditions were kept constant. For the D_0 stage, two sets of experiments were completed. The first set involved quenching the reaction after the set retention time with a measured amount of sodium sulfite to consume the remaining chlorine dioxide. These pulps were then treated in a subsequent extraction stage at constant conditions. The second set of D_0 experiments was done without quenching, but at the end of the retention time a filtrate sample was withdrawn and the residual ClO_2 measured. The bleaching conditions are shown in Table I.

The results of the laboratory trials with the D_0^R residual ClO_2, the D_0^RE kappa number, and ISO brightness as a function of retention time are summarized in Table II, and the detailed results are shown in Appendix B. The bleaching efficiency can be measured as the reduction in kappa number per unit of bleach chemical consumed and is shown as "Δkappa/TAC (% total active chlorine) consumed." The ClO_2 residual as a function of the retention time is shown in Figure 3, while the D_0E kappa number and brightness are shown in Figure 4 for SW. The corresponding results for HW are shown in Figure 5 and Figure 6. The kappa number reduction and ClO_2 consumption is significant after only 30 seconds for both SW and HW with only small changes for the later retention times. The reduction in kappa number for the SW is not quite as large as was seen in the mill trials, indicating that the mixing in the mill was more efficient. This comparison between the mill and lab trials shows that what can be done in the mill can match or exceed the results achieved in the lab with comparable bleaching conditions.

Table I. D_0^RE Bleaching Conditions for Experiments on SW and HW Mill Kraft Pulps

	SW	HW
Initial Kappa Number	28.5	15.3
Kappa Factor	0.16	0.23
Black Liquor, kg/t	10.3	22.0
D_0^R Temperature, °C	45	45
D_0^R Consistency, %	3.3	3.3
D_0^R Time, seconds	30, 60, 120	30, 60, 120
ClO_2, % on odp	1.73	1.34
Quenching Agent	Na_2SO_3	Na_2SO_3
Washing After D_o^R	complete	complete
E Temperature, °C	70	70
E Consistency, %	10	10
E Time, minutes	60	60
NaOH in E, % on odp	2.87	1.76

Table II. Results for Lab D_0^RE Bleaching of SW and HW Mill Kraft Pulps

	SW	0.16 KF		HW		0.23 KF
D_0^R Time, sec.	30	60	120	30	60	120
Initial ClO_2, %	1.73	1.73	1.73	1.34	1.34	1.34
Residual ClO_2, %	0.29	0.25	0.19	0.58	0.50	0.43
ClO_2 Consumed, %	83.5	85.4	89.0	56.7	62.5	67.6
D_0^RE ISO Brightness	38.2	38.6	40.1	50.8	51.0	52.1
D_0^RE Kappa Number	11.7	11.2	10.5	7.5	7.3	6.9
ΔK /TAC Consumed	4.41	4.45	4.45	3.89	3.63	3.53

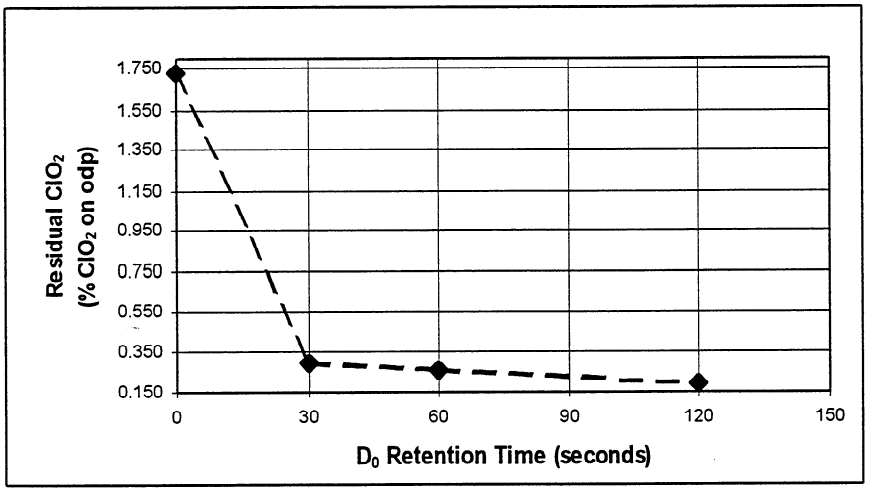

Figure 3. Residual ClO_2 vs. Retention Time for Lab Trials of SW Mill Pulp

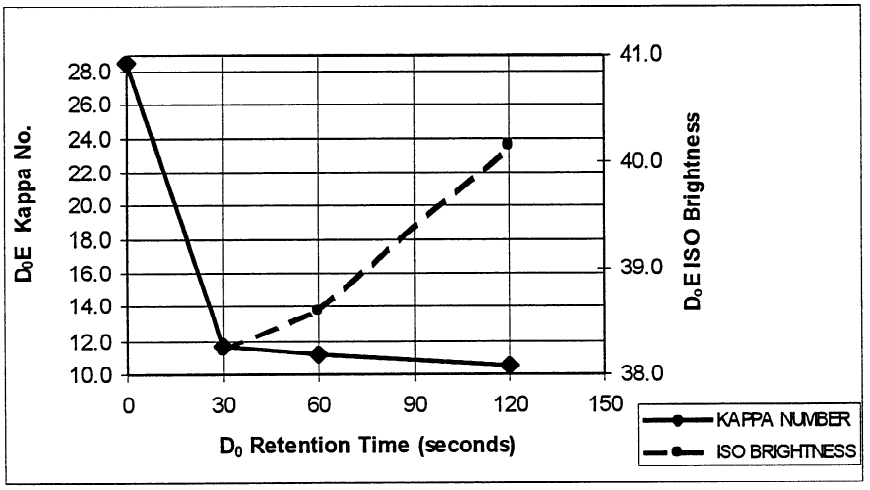

Figure 4. D_0E Kappa Number and Brightness vs. Retention Time for Lab Trials of Mill SW Pulp

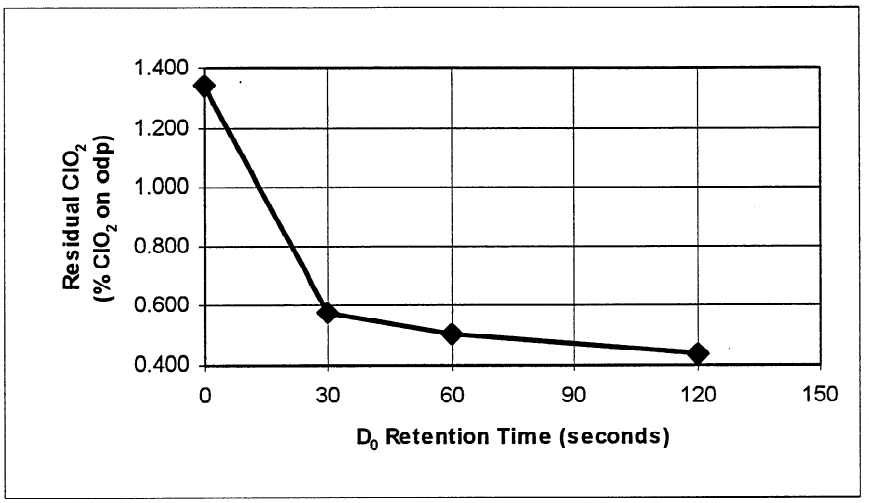

Figure 5. Residual ClO_2 for Lab Trials of HW Mill Pulp

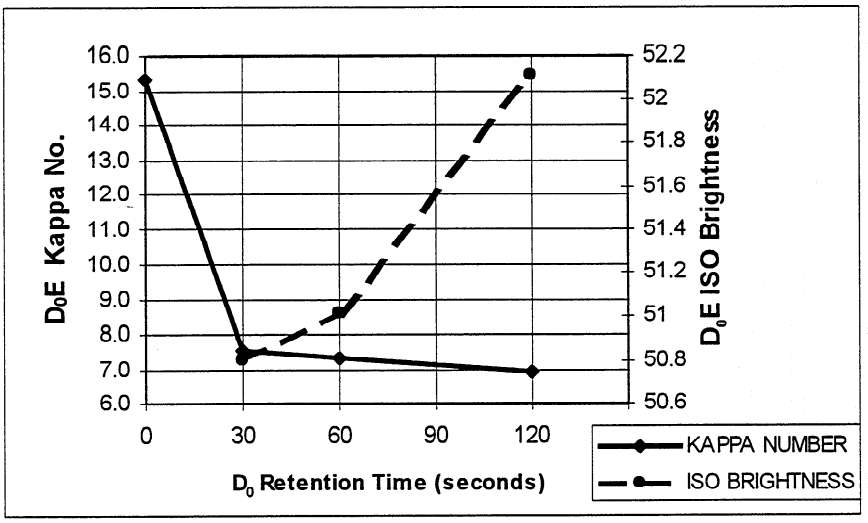

Figure 6. D_0E Kappa Number and Brightness for Lab Trials of Mill HW Pulp

D_0^RE Trials on Laboratory Pulps

Laboratory kraft pulps were made from both loblolly pine (kappa number 29.1) and sweetgum (kappa number 15.6) chip samples. Initial D_0^RE trials on both pulp samples were done at 0.10 kappa factor (KF) at retention times of 30, 60, and 120 seconds in D_0. The bleaching conditions are shown in Table III, and a summary of the results is shown in Table IV. All of the bleaching data are shown in Appendix C. As was seen with the mill pulps, a significant portion of the kappa number reduction was achieved after 30 seconds. After 120 seconds, the reduction in the kappa number was only slightly greater. The consumption of ClO_2 was also significant after 30 seconds, 94% for the pine and 81% for the sweetgum, at the low KF. The bleaching efficiency at this low kappa factor was higher than what was seen with the mill pulps. The kappa numbers after the E stage, however, made it apparent that, at such a low KF, high brightness would require excessive chemical consumption in subsequent DED stages.

Table III. D_0^RE Bleaching Conditions for Laboratory Kraft Pulps, 0.10 KF

	Pine	Sweetgum
Initial Kappa Number	29.1	15.6
Kappa Factor	0.10	0.10
Black Liquor, kg/t	n/a	n/a
D_0^R Temperature, °C	45	45
D_0^R Consistency, %	3.3	3.3
D_0^R Time, seconds	30, 60, 120	30, 60, 120
ClO_2, % on odup	1.11	0.59
Quenching Agent	Na_2SO_3	Na_2SO_3
Washing After D_0^R	complete	complete
E Temperature, °C	70	70
E Consistency, %	10	10
E Time, minutes	60	60
NaOH in E, % on odup	2.18	1.36

Table IV. Results from D_0^RE Bleaching of Laboratory Kraft Pulps, 0.10 KF

	Pine			Sweetgum		
D_0^R Time, seconds	30	60	120	30	60	120
Initial ClO_2, %	1.11	1.11	1.11	0.59	0.59	0.59
Residual ClO_2, %	0.072	0.056	0.036	0.11	0.09	0.07
ClO_2 Consumed, %	93.5	95.0	96.7	80.6	84.5	87.9
D_0^RE ISO Brightness	35.9	36.3	37.0	48.1	49.2	50.7
D_0^RE Kappa Number	13.2	13.1	12.7	8.9	8.5	8.4
ΔK /TAC Consumed	5.85	5.79	5.83	5.35	5.36	5.29

D_0^R(EPO) Trials on Laboratory Pulps

Further trials were done to reach a lower extracted kappa number so that the pulps could be fully bleached. For these, the KF was increased to 0.15 and the D_0^R temperature was increased to 70°C from 45°C. An oxygen and peroxide reinforced extraction (EPO) stage was also used.

The conditions for the D_0^R(EPO) trials are shown in Table V, and the results are shown in Table VI. The bleaching data are shown in Appendix D. For these trials, D_0^R retention times of 60 and 240 seconds were used. Nearly all of the ClO_2 is consumed in the first minute, and significantly lower kappa numbers are reached with these conditions. The bleaching efficiency is lower, especially for the sweetgum, compared to the efficiency at 0.10 KF.

Table V. D_0^R(EPO) Bleaching Conditions for Laboratory Kraft Pulps, 0.15 KF

	Pine	Sweetgum
Initial Kappa Number	29.1	15.2
Kappa Factor	0.15	0.15
Black Liquor, kg/t	n/a	n/a
D_0^R Temperature, °C	70	70
D_0^R Consistency, %	3.3	3.3
D_0^R Time, seconds	60, 240	60, 240
ClO_2, % on odup	1.66	0.87
Quenching Agent	Na_2SO_3	Na_2SO_3
Washing After D_o^r	complete	Complete
EPO Temperature, °C	80	80
EPO Consistency, %	10	10
EPO Time, minutes	60	60
NaOH, % on odup	2.84	2.26
H_2O_2, % on odup	0.80	0.80
O_2	60 psig to 1 atm in 30 min.	

Table VI. Results from D_0^R(EPO) Bleaching of Laboratory Kraft Pulps, 0.15 KF

	Pine		Sweetgum	
D_0^R Time, seconds	60	240	60	240
Initial ClO_2, %	1.66	1.66	0.87	0.87
Residual ClO_2, %	0.023	0.006	0.048	0.004
ClO_2 Consumed, %	98.6	99.6	94.4	99.5
D_0^R(EPO) ISO Brightness	56.2	56.8	69.4	71.6
D_0^R(EPO) Kappa Number	6.6	6.3	6.1	5.9
ΔK /TAC Consumed	5.23	5.24	4.21	4.09
Residual H_2O_2	0	0	0	0

A series of experiments was done using NaOH rather than Na_2SO_3 to quench the D_0^R stage. Another set of experiments on the effect of filtrate carryover from the D_0^R stage into the (EPO) was also done.

The conditions for the trials done with NaOH quenching are shown in Table VII. A 60-second retention time was used. The conditions are the same as those used previously (Table V) except for the use of NaOH for quenching and filtrate carryover. The detailed bleaching data are shown in Appendix D. The kappa number was reduced by 24% for the pine and 5% for the sweetgum compared to the trials with Na_2SO_3 as a quenching agent and no carryover. The bleaching efficiency was increased slightly, assuming that the ClO_2 consumption was the same as that shown in Table VI for the 60-second trial. With 10% carryover, the (EPO) kappa number was slightly higher for both the pine and sweetgum.

Table VII. D_0^R(EPO) Bleaching Conditions for Laboratory Kraft Pulps with NaOH Quenching

	Pine	Sweetgum
Initial Kappa Number	29.1	15.2
Kappa Factor	0.15	0.15
Black Liquor, kg/t	N/a	n/a
D_0^R Temperature, °C	70	70
D_0^R Consistency, %	3.3	3.3
D_0^R Time, seconds	60	60
ClO_2,% on odup	1.66	0.87
Quenching Agent -NaOH	1.81%	1.15%
Washing After D_0^R	Complete/10% carryover	Complete/10% carryover
(EPO) Temperature, °C	80	80
(EPO) Consistency, %	10	10
(EPO) Time, minutes	60	60
NaOH, % on odup	2.84	2.33
H_2O_2, % on odup	0.80	0.80
O_2	60 psig to 1 atm in 30 min.	

Table VIII. Results from D_0^R(EPO) Bleaching of Laboratory Kraft Pulps with NaOH Quenching

	Pine		Sweetgum	
Filtrate carryover to (EPO)	0%	10%	0%	10%
D_0^R Time, seconds	60	60	60	60
Initial ClO_2, %	1.66	1.66	0.87	0.87
D_0^R Exit pH	7.40	8.05	7.90	7.70
D_0^R(EPO) ISO Brightness	52.8	50.1	69.7	67.6
D_0^R(EPO) Kappa Number	5.9	6.4	5.8	5.9
ΔK /TAC Consumed	5.39	5.27	4.36	4.11
Residual H_2O_2	0	0	0	0

A summary of the extraction stage kappa numbers as a function of the D_0 retention time is shown in Figure 7 for the lab pine pulps and in Figure 8 for the lab sweetgum pulps. An acceptable kappa number of 5 to 6 that would allow for further bleaching without excessive chemical was achieved in only 60 seconds in the D_0 stage when the KF was 0.15 and an (EPO) stage was used. There was not a significant effect from filtrate carryover or when using either NaOH or Na_2SO_3 for quenching. A 30-minute (1800 secs.) D_0 resulted in only a slight further reduction in the kappa number in both cases.

The conditions shown in Table VII with 10% carryover were chosen to produce D_0^R(EPO) pulps for further testing with the (D/E/D) final bleaching stages.

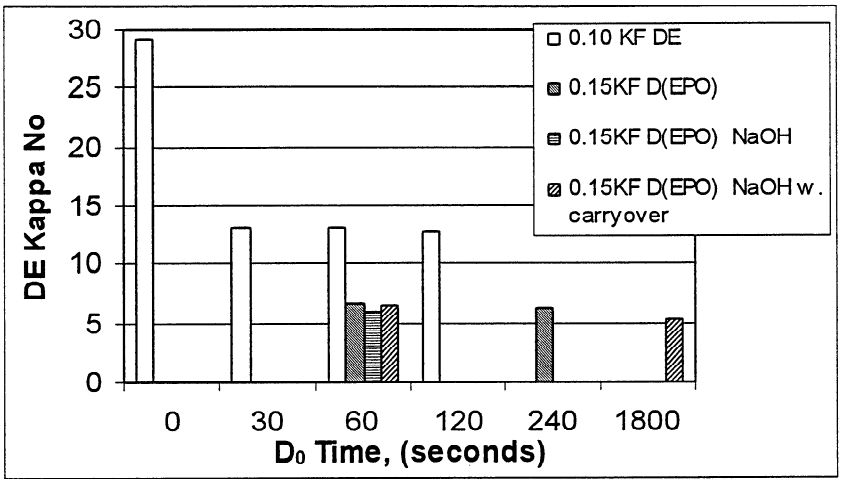

Figure 7. Extracted Kappa Number vs. D_0 Retention Time for Pine Pulps

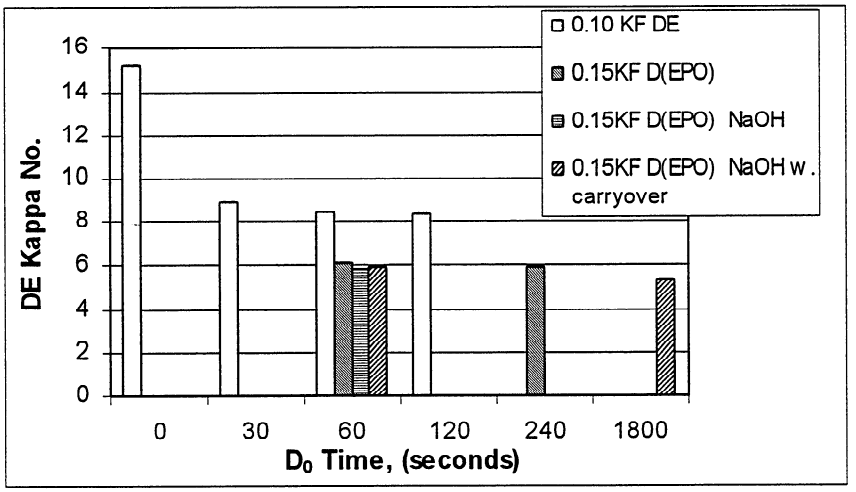

Figure 8. Extracted Kappa Number vs. D_0 Retention Time for Sweetgum Pulps

(D/E/D) Stages with Short-Retention 8-minute D_1

A large batch of pulp was made for optimization of the (D/E/D) stages by running multiple D_0^R(EPO) stages according to the conditions in Table VII with 10% carryover into the (EPO) stage. The (EPO) pulps were then combined and portions were used for selected trials with (D/E/D).

The bleaching conditions used for the initial trials are shown in Table IX. The D_1 stage was initially done with a short retention time of 8 minutes as suggested by Histed in his "simplified bleaching" scheme. For these (D/E/D) trials, three levels of ClO_2 were used in D_1 and each of these was further bleached with three levels of ClO_2 in the D_2 stage. The (D/E/D) results are summarized in Table X for the pine pulp and in Table XI for the sweetgum pulp. The detailed bleaching data are shown in Appendix E.

Table IX. Bleaching Conditions for (D/E/D) Stages with 8 min. D_1

	D_1	E	D_2
Temperature, °C	80	80	80
Consistency, %	10	10	variable
Time, minutes	8	4	variable,180 max
Carryover	20% from (EPO)	100% from D_1	100% from E
Chemical	ClO_2	conc. NaOH	ClO_2
% on odp	1.0, 1.5, 2.0	variable	0.25, 0.50, 1.0

Table X. Results for (D/E/D) Bleaching of Pine Pulp with 8 min. D_1

D_1 %ClO_2	1.0			1.5			2.0		
D_1 Residual	0.02			0.13			0.33		
D_1 Brightness	75.3			79.6			81.5		
Brightness Reversion	-7.0			-7.2			-6.6		
D_2 %ClO_2	0.25	0.50	1.0	0.25	0.50	1.0	0.25	0.50	1.0
D_2 Residual	0	0	0	0	0	0	0	0	0
D_2 Brightness	80.1	82.2	85.4	83.6	84.9	87.0	86.3	86.5	87.7
Brightness Reversion	-3.6	-3.6	-3.5	-3.9	-3.4	-3.1	-3.1	-2.8	-2.6
Viscosity, mPa.s	16.2	15.9	14.9	14.8	13.8	14.1	11.4	11.2	11.5
D_0 -1.58% ClO_2 ;(EPO) Kappa number 6.0; (EPO) brightness 50.6; (EPO) viscosity 16.8									

Table XI. Results for (D/E/D) Bleaching of Sweetgum Pulp with 8 min. D_1

D_1 %ClO_2	1.0			1.5			2.0		
D_1 Residual	0.15			0.12			0.22		
D_1 Brightness	85.6			85.9			86.3		
Brightness Reversion	-7.8			-6.5			-7.7		
D_2 %ClO_2	0.25	0.50	1.0	0.25	0.50	1.0	0.25	0.50	1.0
D_2 Residual	0	0	0	0	0	0	0	0	0
D_2 Brightness	89.0	89.9	90.4	89.4	90.0	91.0	89.9	90.6	90.4
Brightness Reversion	-5.0	-4.9	-4.4	-4.0	-3.8	-3.7	-4.5	-4.8	-3.8
Viscosity, mPa.s	16.3								
D_0 -0.86% ClO_2 ;(EPO) Kappa number 5.5; (EPO) brightness 68.2; (EPO) viscosity 18.4									

D(EPO)D Sequence

A control sequence, D(EPO)D, with a 30-min. D_0 was done for a comparison to the D_0^R(EPO)(D/E/D) results. A series of trials were done with target levels of 0.30, 0.60, 1.2, and 2.4% ClO_2 added in the D_1 stage. The bleaching conditions are shown in Table XII. The bleaching results for the control sequence are summarized in Table XIII for pine and in Table XIV for sweetgum. The detailed data are shown in Appendix F.

Table XII. Conditions for D(EPO)D Control Sequence

	D_0	(EPO)	D_1
Temperature, °C	70	80	80
Consistency, %	3.3	10	10
Time, minutes	30	4	variable,180 max
Carryover		10% from D_0	20% from (EPO)
Chemical	ClO_2	NaOH/ H_2O_2	ClO_2
% on odp	0.15 KF	Variable/0.8%	0.30, 0.60, 1.2, 2.4%

Table XIII. Results of D(EPO)D Sequence on Pine

D_1 %ClO_2	0.30	0.60	1.2	2.4
D_1 Residual %odp	0	0	0	0.02
D_1 Brightness	66.6	70.4	81.0	86.1
D_1 Brightness Reversion	-5.8	-5.1	-6.0	-4.7
Viscosity, mPa.s	15.8	15.9	16.4	15.9
D_0 -1.59% ClO_2 ;(EPO) Kappa number 5.3; (EPO) brightness 58.0; (EPO) viscosity 18.3				

Table XIV. Results of D(EPO)D Sequence on Sweetgum

D_1 %ClO_2	0.30	0.60	1.2	2.4
D_1 Residual %odp	0	0	0	0
D_1 Brightness	80.9	83.8	85.3	89.2
D_1 Brightness Reversion	-7.2	-6.6	-5.3	-4.8
Viscosity, mPa.s	12.7	12.4	12.6	8.7
D_0 -0.85% ClO_2 ;(EPO) Kappa number 5.3; (EPO) brightness 71.9; (EPO) viscosity 15.2				

The brightness results as a function of the total ClO_2 applied for both the D(EPO)D (control) and D^R(EPO)(D/E/D) (test) sequences are shown in Figure 9 for pine and in Figure 10 for sweetgum.

For the pine pulp, the test and control sequences reach a brightness of 85 at the same total applied ClO_2 of 3.6%. It appears that a brightness ceiling of about 87-88 is reached on the pine. The test sequence does exhibit a better brightness stability since the brightness reversion is not as great as the control sequence.

For the sweetgum pulp, the test sequence has a distinct advantage over the control sequence and is able to reach a brightness of 89 with 2.1% applied ClO_2 compared to 3.2% ClO_2 for the control sequence. The viscosity for the test sequence is also much higher at 89 brightness than the control. The brightness reversion at 89 brightness is similar for the two sequences.

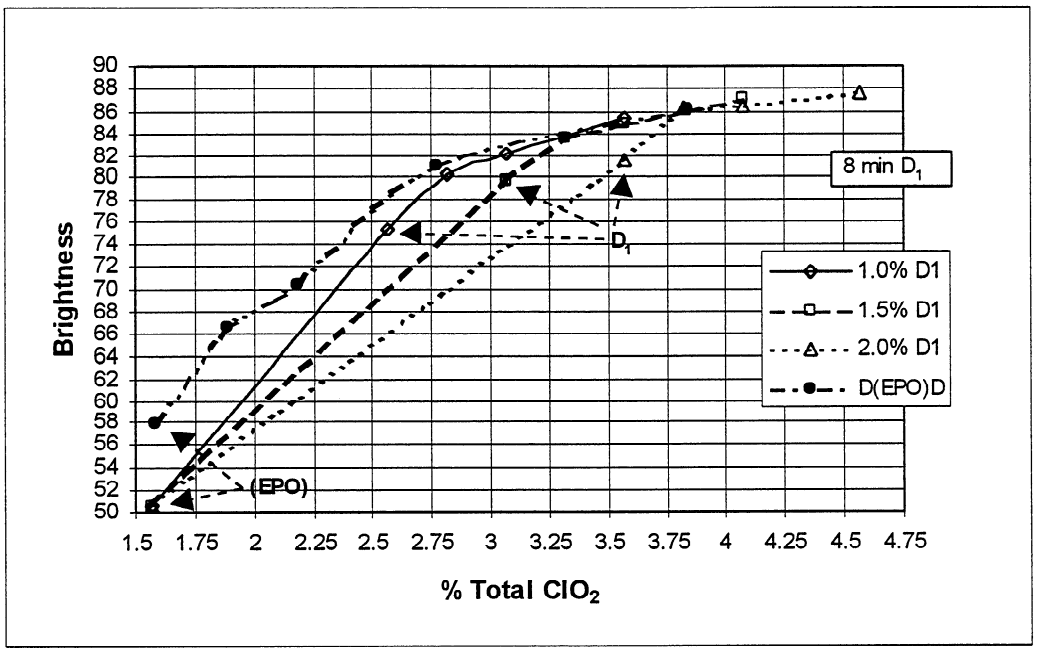

Figure 9. Final Brightness vs. %Total ClO_2 Applied for D(EPO)D and D^R(EPO)(D/E/D) Sequences on Pine

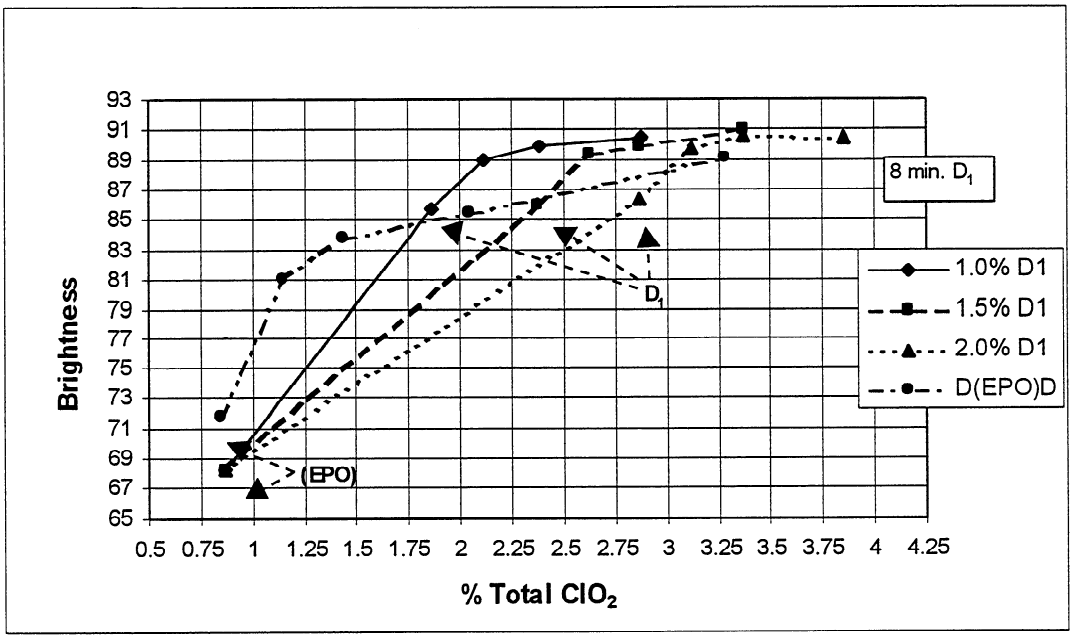

Figure 10. Final Brightness vs. %Total ClO_2 Applied for D(EPO)D and D^R(EPO)(D/E/D) Sequences on Sweetgum

(D/E/D) Stages with 60-Minute D_1

Another series of (D/E/D) experiments were done where the D_1 retention time was increased to 60 minutes from 8 minutes to see if there was an advantage in bleaching response. This would be feasible in a mill that is converting a CED bleach plant since the C tower could be used for the D_1 stage.

The results for bleaching the sweetgum sample with the 60-minute D_1 stage are shown in Table XV, while the detailed data is included in Appendix E. The D_0^R(EPO) conditions are the same as those in Table VII with 10% carryover, and the (D/E/D) conditions are the same as those in Table IX, except for the longer D_1 time. For these trials, the brightness after the D_1 stage with 1% ClO_2 was 3 points lower than after the corresponding 8-minute D_1 stage in Table XI. At 1.5% ClO_2, the brightness for the 60-minute stage was 1.4 points lower. At 2.0% ClO_2, the 60-minute D_1 was 1.6 points higher. It is evident that with the combination of a longer time and a temperature of 80°C, there is some reversion occurring at the lower ClO_2 doses.

Table XV. Results for (D/E/D) Bleaching of Sweetgum Pulp with 60 min., 80°C D_1

D_1 %ClO_2	1.0			1.5			2.0		
D_1 Residual	0			0			0		
D_1 brightness	82.5			84.5			87.6		
Brightness Reversion	-6.1			-5.3			-5.3		
D_2 %ClO_2	0.25	0.50	1.0	0.25	0.50	1.0	0.25	0.50	1.0
D_2 Residual	0	0	0	0	0	0	0	0	0
D_2 Brightness	87.9	88.5	88.6	89.1	89.7	89.0	89.7	90.6	91.3
Brightness Reversion	-4.5	-4.6	-4.5	-3.7	-3.7	-2.0	-3.9	-3.6	-3.3
Viscosity, mPa.s	14.4	14.5	14.0	10.2	10.2	10.8	8.4	8.3	8.2
D_0 -0.86% ClO_2 ;(EPO) Kappa number 5.4; (EPO) brightness 67.1; (EPO) viscosity 16.0									

A series of tests were then done to explore the effect of a lower temperature with a 60-minute D_1 stage. Temperatures of 50, 60, and 70°C were used for the D_1 stage. The results, shown in Table XVI indicate that up to 70°C, there is still a measurable residual as well as a brightness increase. The 87.9 brightness for the sweetgum is substantially better than the 82.5 brightness with 1.0% ClO_2 at 80°C. The brightness values at 70°C and 60 minutes are also significantly higher than the 1% D_1 brightness values for the 8-minute, 80°C stages in Table X and Table XI.

Table XVI. Results for D_0^R(EPO)D Bleaching with Different D_1 Temperatures

	Pine			Sweetgum		
Temperature, °C	50	60	70	50	60	70
D_1 Time, min.	60	60	60	60	60	60
D_1 %ClO_2	1.0	1.0	1.0	1.0	1.0	1.0
D_1 Residual, %odp	0.10	0.09	0.06	0.28	0.13	Trace
D_1 Brightness	79.8	80.2	80.5	85.0	86.0	87.9

A D_1 temperature of 70°C was chosen for subsequent work, and some additional trials were done to optimize the D_2 dosage with these D_1 conditions for the pine pulp. The

results are shown in Table XVII and the detailed bleach data in Appendix E. For these trials, a new batch of pine pulp had to be made from the same chip source. The kappa number of 25.8 for this second batch of pulp was less than the kappa number of 29.1 for the pine pulp used for the previous testing. In this case, a brightness of 85 was reached with a total of 2.75% ClO_2 applied.

Table XVII. Results for D_2 Optimization of Pine with 60 Min., 70°C D_1

Initial Kappa Number	25.8		
Initial Viscosity	26.7		
D_0 %ClO_2	1.52		
(EPO) Kappa Number	4.8		
D_1 %ClO_2	1.0		
D_1 Residual	0		
D_1 Brightness	80.8		
Brightness Reversion	-7.1		
D_2 %ClO_2	0.25	0.50	1.0
D_2 Residual	0	0	0
D_2 Brightness	84.9	86.3	88.4
Brightness Reversion	-4.2	-4.0	-3.4
Viscosity, mPa.s	13.4	13.4	13.1

The brightness response as a function of the total ClO_2 applied for each of the complete bleaching sequences is shown in Figure 11 for the sweetgum pulp and Figure 12 for the pine pulp. The D^R(EPO)(D/E/D) results for the sweetgum show the higher brightness that was achieved for the 8-minute, 80°C D_1 stages compared to the 60-minute, 80°C stages at the 1.0 and 1.5% ClO_2 levels. This was due to brightness reversion during the longer time at 80°C. For either of the test sequences, however, the brightness response was significantly better than the control. For the D^R(EPO)(D/E/D) pine pulp, the 60-minute D_1 stages were done at 70°C and show an improvement of 3-5 points in brightness response compared to the 8-minute, 80°C stages. There was a similar improvement over the control sequence.

Bleached Pulps for Strength and Filtrate Testing

Separate bleached pulps were prepared with ClO_2 applications that would result in a brightness of 85 for pine and 88 for sweetgum. For the test sequence, pulps were prepared with both 8-minute, 80°C and 60-minute, 70°C D_1 stages. The final brightness values of these pulps are also shown in Figure 11 and Figure 12 as single points. They compare well to the corresponding pulps made with the same conditions during the optimization testing, indicating good reproducibility.

The bleaching conditions and results for the pine pulps used for strength and filtrate testing are shown in Table XVIII and in Table XIX for the sweetgum pulps. The complete results for the test sequence pulps are shown in Appendix E and in Appendix F for the control pulps.

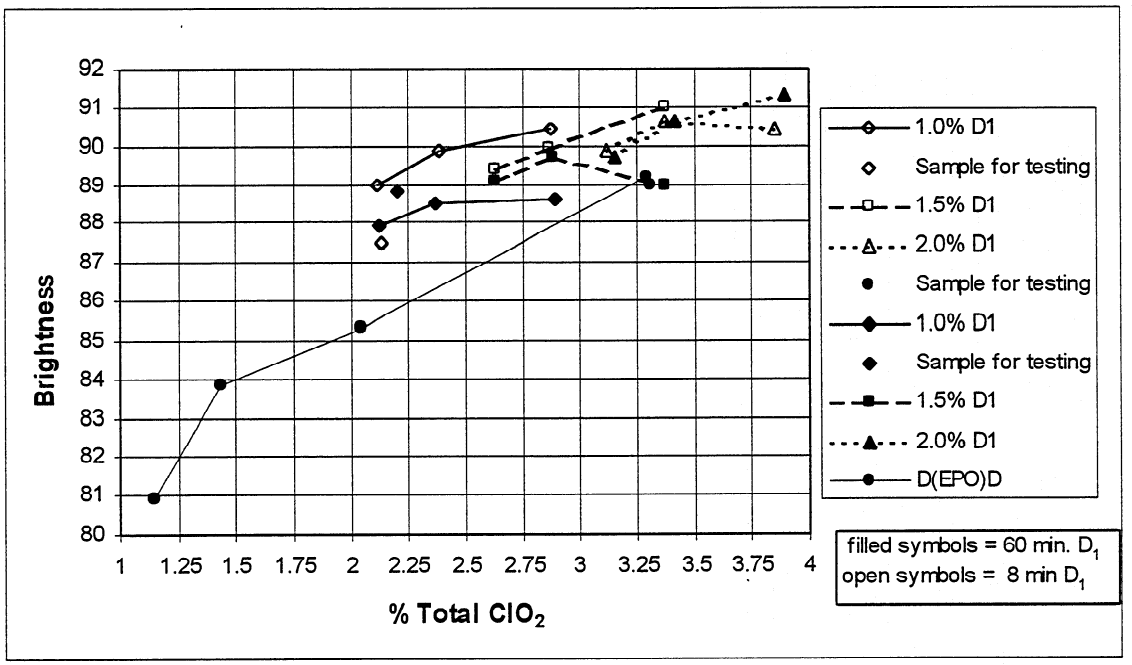

Figure 11. Results for D^R(EPO)(D/E/D) and D(EPO)D Bleaching of Sweetgum

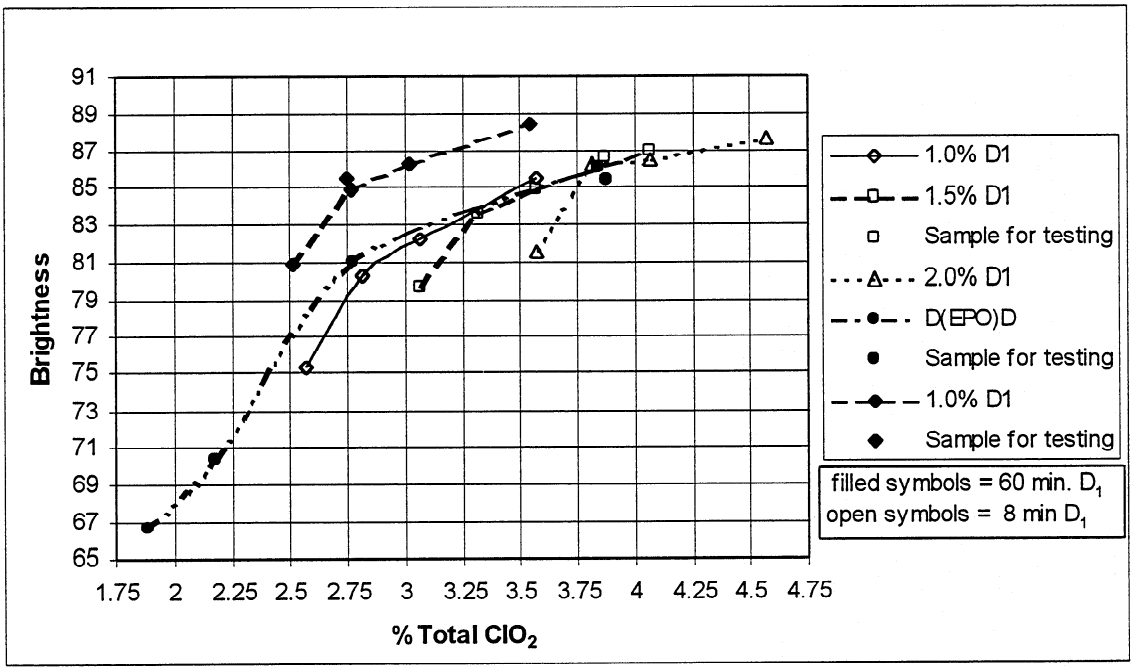

Figure 12. Results for D^R(EPO)(D/E/D) and D(EPO)D Bleaching of Pine

Table XVIII. Bleaching Results for Pine Pulps Used for Testing

Sequence	D^R(EPO)(D/E/D)	D^R(EPO)(D/E/D)	D(EPO)D
Initial Kappa Number	28.2	25.8	25.8
Initial Viscosity, m.Pa.s	25.0	26.7	26.7
D_0 %ClO_2	1.62	1.51	1.53
D_0 Time, min.	1	1	30
(EPO) Kappa Number	6.1	4.8	4.4
D_1 %ClO_2	1.46	0.97	2.35
D_1 Time, min.	8	60	120
D_1 Temperature °C	80	70	80
D_1 Brightness	77.4	82.0	85.3
D_1 Brightness Reversion	-3.2	-7.1	-4.9
D_2 %ClO_2	0.79	0.27	
D_2 Time, min.	90	35	
D_2 Brightness	86.6	85.5	
D_2 Brightness Reversion	-3.6	-4.1	
Final Viscosity, m.Pa.s	15.8	12.4	11.2
Total %ClO_2 Applied	3.87	2.75	3.88
Combined AOX, kg/ADMT	0.73	0.55	0.69

Table XIX. Bleaching Results for Sweetgum Pulps Used for Testing

Sequence	D^R(EPO)(D/E/D)	D^R(EPO)(D/E/D)	D(EPO)D
Initial Kappa Number	15.2	15.2	15.2
Initial Viscosity, m.Pa.s	29.2	29.2	29.2
D_0 %ClO_2	0.85	0.85	0.86
D_0 Time, min.	1	1	30
(EPO) Kappa Number	5.9	5.7	4.9
D_1 %ClO_2	0.99	1.0	2.45
D_1 Time, min.	8	60	95
D_1 Temperature °C	80	70	80
D_1 Brightness	82.5	85.5	89.0
D_1 Brightness Reversion	-8.2	-6.0	-6.0
D_2 %ClO_2	0.29	0.35	
D_2 Time, min.	25	30	
D_2 Brightness	87.5	88.8	
D_2 Brightness Reversion	-4.9	-3.8	
Final Viscosity, m.Pa.s	16.7	15.8	9.6
Total %ClO_2 Applied	2.13	2.20	3.31
Combined AOX, kg/ADMT	0.39	0.42	0.61

For the pine pulps, the total ClO_2 applied was 3.9% for the test sequence with the 8-minute, 80°C D_1 stage and 2.8% for the same sequence with the 60-minute, 70°C D_1 stage. The control sequence required 3.9% ClO_2 to reach the target brightness of 85. The control sequence also had a lower final viscosity than the two test-sequence pulps.

For the sweetgum, the total ClO_2 applied for the test sequence with the 8-minute, 80°C D_1 stage was 2.1% and 2.2% for the test sequence with the 60-minute, 70°C D_1 stage. For the control sequence, 3.3% ClO_2 was required to reach 88 brightness. The viscosity of the control pulp was also significantly less than the test-sequence pulps.

The AOX of the combined filtrate for the sequence corresponds to the total ClO_2 applied for the sequence. The lower ClO_2 required to reach the target brightness for the test sequence results in a lower AOX production.

The strength results at a freeness of 400 are shown in Table XX. The complete strength results are shown in Appendix G. The test sequence resulted in a higher tensile and burst strength for the pine pulp than the control and a similar tear strength. For the sweetgum pulp, the test sequence resulted in significantly better strength than the control sequence.

Table XX. Strength Results at 400 CSF

Sequence	D^R(EPO)(D/E/D)	D^R(EPO)(D/E/D)	D(EPO)D
Pine	8 min. D_1	60 min. D_1	
Tensile Index	73.5	75.5	68.5
Burst Index	6.55	6.21	6.05
Tear Index	13.5	12.3	12.5
Zero Span Tensile Index	133	113	120
Sweet Gum			
Tensile Index	54	55	49
Burst Index	3.7	3.7	3.35
Tear Index	10.4	10.2	8.8
Zero Span Tensile Index	131	115	99

The tear strength as a function of the tensile strength is shown in Figure 13 for the pine pulp. The test sequence with the 8-minute D_1 stage has a higher tear at a given tensile while the 60-minute D_1 test sequence and the control had similar results.

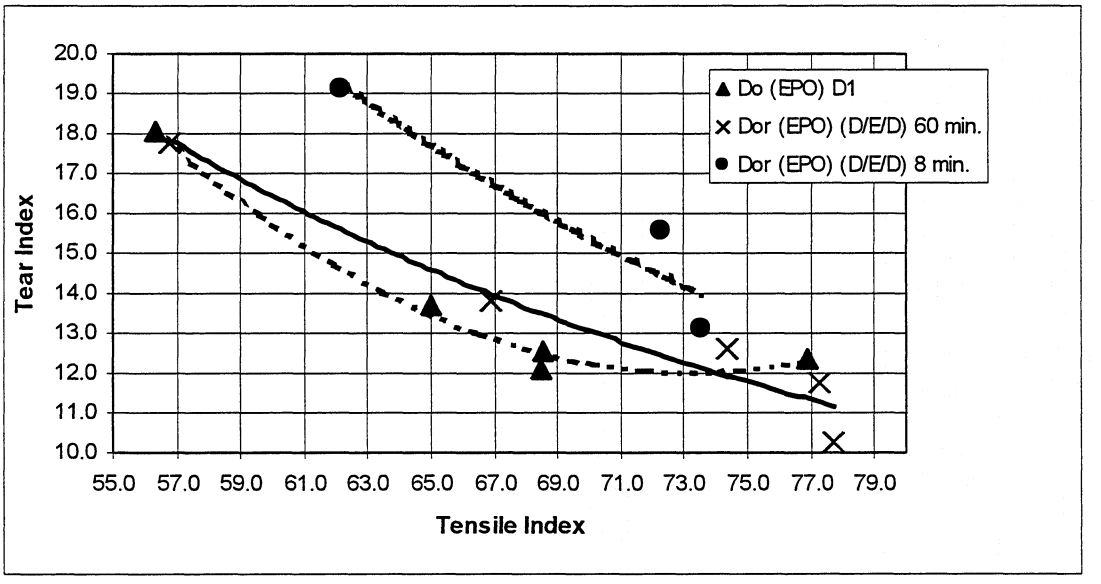

Figure 13. Tear vs. Tensile Strength for Pine Pulp

The tear strength versus the tensile strength for the sweetgum is shown in Figure 14. In this case, the test sequence has a higher tear at a given tensile than the control sequence.

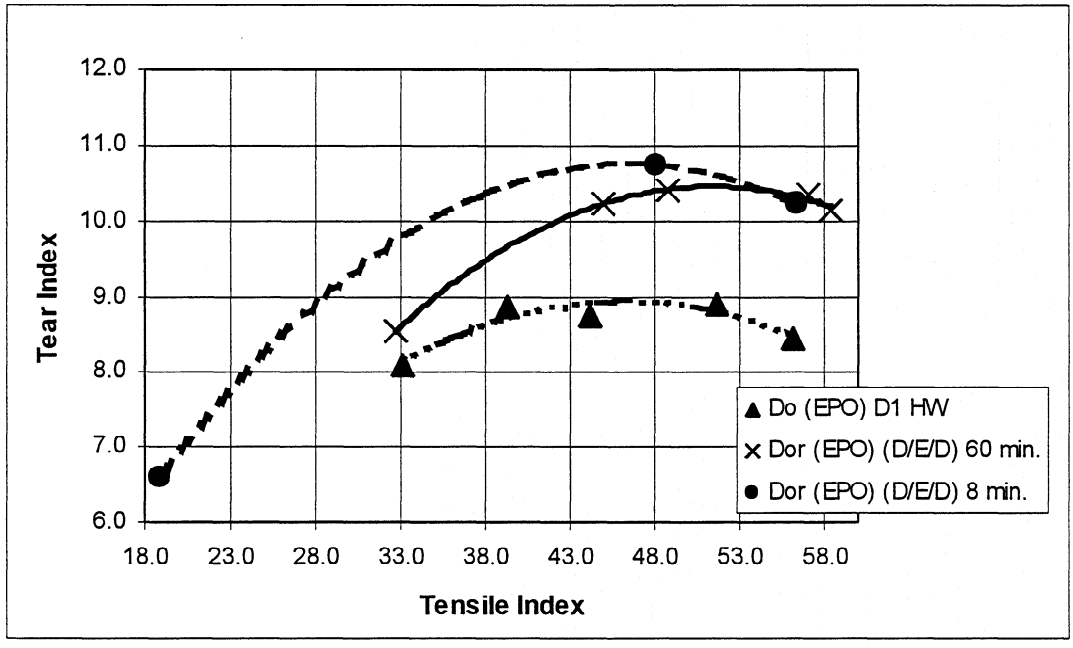

Figure 14. Tear vs. Tensile for Sweetgum Pulp

Conclusions

A comparison between mill and lab trials with a rapid D_0 stage showed that efficient mixing could be achieved in the mill and that the efficiency exceeded what could be done in the lab.

The laboratory study successfully demonstrated the capabilities of the D^R(EPO)(D/E/D) sequence. An existing three- or four-stage bleach plant can be converted to the more powerful D^R(EPO)(D/E/D) sequence without the major capital cost of additional washers. The results from this study showed that the D^R(EPO)(D/E/D) sequence can reach 85 brightness on SW with 2.8% total ClO_2 while the control sequence, D(EPO)D, required 3.9% ClO_2. There was a corresponding decrease in AOX for the test sequence. Pulp strength of the test sequence was similar to or slightly higher than the control. For the HW pulp, the test sequence reached 88 brightness with 2.2% ClO_2 compared to 3.3% ClO_2 for the control. There was a corresponding decrease in AOX generation with the lower chemical requirements. The final viscosity and pulp strength for the test sequence on HW was significantly higher than the control sequence.

Acknowledgements

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Professor

August 7, 2000
Date

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Sr. Associate Engineer

August 7, 2000
Date

Appendix A - Mill Trial Data

Mill Sampling 1/15

SW D_o Stage - Samples collected after #2 mixer.

All ClO_2 added to #1 mixer. Estimated sampling time 45-50 seconds after mixer.

Ave. Prod. rate	275 T/D	Stock consistency	3.30%
ClO_2 Flow	62 gpm	%ClO2	1.63%
Mill Kappa	26.8	Kappa factor	0.16

Bleach line consistency calculated from consistency, production rate, ClO_2 flow = 3.16% cons.

Sample number	Date	Sample time	Retention time after sampling	Chemical added	Vol. chemical added	Water added	Sample weight total	Sample weight net	Sample consistency	E Stage			
										Sample wt.	NaOH	Final pH	Kappa number
			Sec.		mls	mls	g	g	%	g	%		
Brownstock	15-Jan	16:12											27.6
1	15-Jan	15:29	0	Na_2SO_3, 10 g/l	600		2142	1542	2.27%	25	2.17	11.9	8
2	15-Jan	15:30	35	Na_2SO_3, 10 g/l	600		2530	1930	2.41%	25	2.17	11.8	8.1
3	15-Jan	15:32	60	Na_2SO_3, 10 g/l	600		2450	1850	2.39%	25	2.17	11.8	8.1
4	15-Jan	15:33	120	Na_2SO_3, 10 g/l	600		2987	2387	2.53%	25	2.17	11.9	7.4
5	15-Jan	15:36	240	Na_2SO_3, 10 g/l	600		3137	2537	2.56%	25	2.17	11.8	6.9
Mill EO stage	15-Jan	18:18											6.4

Sample number	Date	Sample time	Retention time after sampling	Chemical added	Vol. chemical added	Water added	Sample weight total	Sample weight net	Sample consistency	Filtrate sample	Thio. 0.1 N	Thio. 0.1 N	Residual ClO_2
			sec.		mls	mls	g	g	%	mls	mls	mls	% bop
6	15-Jan	15:38	0	KI 1.0N	100	200	2374	2074	2.76%	50	2.3	2.4	0.22%
7	15-Jan	15:55	30	KI 1.0N	100	200	2687	2387	2.81%	50	2.1		0.20%
8	15-Jan	15:56	60	KI 1.0N	100	200	2340	2040	2.75%	50	1.9		0.18%
9	15-Jan	15:59	120	KI 1.0N	100	200	2615	2315	2.80%	50	1.1	1.3	0.11%
10	15-Jan	16:02	240	KI 1.0N	100	200	2840	2540	2.83%	50	1	1	0.09%

Mill Sampling 1/16

SW D_o Stage - Samples collected after #2 mixer.

All ClO_2 added to #2 mixer. Estimated sampling time 29 seconds after mixer.

Ave. Prod. Rate 275 T/D

Stock Consistency 3.30%

ClO_2 Flow 62 gpm

Bleach line consistency calculated from consistency, production rate, ClO_2 flow = 3.16% cons.

Sample number	Date	Sample time	Retention time after sampling	Chemical added	Vol. chemical added	Water added	Sample weight total	Sample weight net	Sample consistency	E Stage			
										Sample wt.	NaOH	Final pH	Kappa number
			sec.		mls	mls	g	g	%	g	%		
Brownstock	16-Jan	11:00											27.5
1	16-Jan	8:50	0	Na_2SO_3, 10 g/l	600		2931	2331	2.51%	25	2.17	11.9	9.2
2	16-Jan	8:51	35	Na_2SO_3, 10 g/l	600		2842	2242	2.49%	25	2.17	11.8	8.9
3	16-Jan	8:53	60	Na_2SO_3, 10 g/l	600		2580	1980	2.43%	25	2.17	11.8	8.6
4	16-Jan	8:55	120	Na_2SO_3, 10 g/l	600		3176	2576	2.56%	25	2.17	11.9	8.4
5	16-Jan	8:58	240	Na_2SO_3, 10 g/l	600		2920	2320	2.51%	25	2.17	11.8	7.9
11	16-Jan	10:02	0	Na_2SO_3, 10 g/l	1500		6188	4688	2.39%	25	2.17		11.1
Mill EO stage	16-Jan	11:40											6.4

Sample number	Date	Sample time	Retention time after sampling	Chemical added	Vol. chemical added	Water added	Sample weight total	Sample weight net	Sample consistency	Filtrate sample	Thio. 0.1 N	Thio. 0.1 N	Residual ClO_2
			sec.		mls	mls	g	g	%	mls	mls	mls	% bop
6	16-Jan	9:00	0	KI 1.0N	100	200	2678	2378	2.81%	50	2.9	2.8	0.27%
7	16-Jan	9:03	30	KI 1.0N	100	200	2338	2038	2.75%	50	2.4	2.4	0.23%
8	16-Jan	9:06	60	KI 1.0N	100	200	2708	2408	2.81%	50	2.1		0.20%
9	16-Jan	9:08	120	KI 1.0N	100	200	2664	2364	2.80%	50	1.4	1.4	0.13%
10	16-Jan	9:11	240	KI 1.0N	100	200	2684	2384	2.81%	50	1	1	0.09%
12	16-Jan	10:40	0	KI 1.0N	300	600	5612	4712	2.65%	50	2	2.1	0.20%

Appendix B - Lab Bleaching Data for Mill Pulps

D_0^RE Bleaching of Mill SW Pulp

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO
KF=0.16	Initial	Mill SW							28.5	
D (residual)	D	3.3	0.5	45	1.73% ClO_2	1.03% BLS	2.60	0.293		
D (residual)	D	3.3	0.5	45	1.73% ClO_2	1.03% BLS	2.75	0.278		
D (residual)	D	3.3	1	45	1.73% ClO_2	1.03% BLS	2.65	0.266		
D (residual)	D	3.3	1	45	1.73% ClO_2	1.03% BLS	2.75	0.239		
D (residual)	D	3.3	2	45	1.73% ClO_2	1.03% BLS	2.50	0.195		
D (residual)	D	3.3	2	45	1.73% ClO_2	1.03% BLS	2.80	0.188		
D quench E	D	3.3	0.5	45	1.73% ClO_2	1.03% BLS				
	quench				2.67% Na_2SO_3					
	E	10.0	60	70	2.87% NaOH	0	11.35		11.7	38.3
	D	3.3	0.5	45	1.73% ClO_2	1.03% BLS				
	quench				2.67% Na_2SO_3					
	E	10.0	60	70	2.87% NaOH		11.30		11.7	38.2
	D	3.3	1	45	1.73% ClO_2	1.03% BLS				
	quench				2.36% Na_2SO_3					
	E	10.0	60	70	2.87% NaOH	0	11.40		11.0	38.7
	D	3.3	1	45	1.73% ClO_2	1.03% BLS				
	quench				2.36% Na_2SO_3					
	E	10.0	60	70	2.87% NaOH	0	11.35		11.2	38.5
	D	3.3	2	45	1.73% ClO_2	1.03% BLS				
	quench				1.80% Na_2SO_3					
	E	10.0	60	70	2.87% NaOH		11.25		10.4	40.2
	D	3.3	2	45	1.73% ClO_2	1.03% BLS				
	quench				1.80% Na_2SO_3					
	E	10.0	60	70	2.87% NaOH	0	11.35		10.4	40.1

D_0^RE Bleaching of Mill HW Pulp

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO
KF=0.23	Initial	Mill HW							15.3	
D (residual)	D	3.3	0.5	45	1.34% ClO_2	2.20% BLS	2.85	0.578		
D (residual)	D	3.3	0.5	45	1.34% ClO_2	2.20% BLS	2.80	0.580		
D (residual)	D	3.3	1	45	1.34% ClO_2	2.20% BLS	2.85	0.513		
D (residual)	D	3.3	1	45	1.34% ClO_2	2.20% BLS	2.90	0.491		
D (residual)	D	3.3	2	45	1.34% ClO_2	2.20% BLS	2.90	0.430		
D (residual)	D	3.3	2	45	1.34% ClO_2	2.20% BLS	2.90	0.438		
D quench E	D	3.3	0.5	45	1.34% ClO_2	2.20% BLS				
	quench				5.40% Na_2SO_3					
	E	10.0	60	70	1.76% NaOH	0	11.40		7.46	49.8
	D	3.3	0.5	45	1.34% ClO_2	2.20% BLS				
	quench				5.40% Na_2SO_3					
	E	10.0	60	70	1.76% NaOH	0	11.30		7.62	51.8
	D	3.3	1	45	1.34% ClO_2	2.20% BLS				
	quench				4.69% Na_2SO_3					
	E	10.0	60	70	1.76% NaOH	0	11.40		7.32	50.4
	D	3.3	1	45	1.34% ClO_2	2.20% BLS				
	quench				4.69% Na_2SO_3					
	E	10.0	60	70	1.76% NaOH	0	11.30		7.3	51.6
	D	3.3	2	45	1.34% ClO_2	2.20% BLS				
	quench				4.05% Na_2SO_3					
	E	10.0	60	70	1.76% NaOH	0	11.30		6.88	52.5
	D	3.3	2	45	1.34% ClO_2	2.20% BLS				
	quench				4.05% Na_2SO_3					
	E	10.0	60	70	1.76% NaOH	0	11.40		6.94	51.7

Appendix C - D_0^RE Trials on Lab Pulps

D_0^RE Lab Bleaching of Pine Pulp, 0.10 KF

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Final pH	Residual %	Kappa No.	Bright. ISO
KF=0.10	Initial	IPST Loblolly Pine - no carryover						29.1	
D (residual)	D	3.3	0.5	45	1.11% ClO_2	2.70	0.071		
D (residual)		3.3	0.5	45	1.11% ClO_2	2.75	0.073		
D (residual)	D	3.3	1	45	1.11% ClO_2	2.70	0.052		
D (residual)		3.3	1	45	1.11% ClO_2	2.80	0.059		
D (residual)	D	3.3	2	45	1.11% ClO_2	2.70	0.034		
D (residual)	D	3.3	2	45	1.11% ClO_2	2.95	0.038		
D quench E	D	3.3	0.5	70	1.11% ClO_2				
	quench				0.67% Na_2SO_3				
	E	10.0	60	70	2.18% NaOH	11.30	0	13.2	36.2
	D	3.3	0.5	70	1.11% ClO_2				
	quench				0.67% Na_2SO_3				
	E	10.0	60	70	2.18% NaOH	11.25	0	13.2	35.6
	D	3.3	1	70	1.11% ClO_2				
	quench				0.53% Na_2SO_3				
	E	10.0	60	70	2.18% NaOH	11.30	0	13	36.4
	D	3.3	1	70	1.11% ClO_2				
	quench				0.53% Na_2SO_3				
	E	10.0	60	70	2.18% NaOH	11.15	0	13.2	36.2
	D	3.3	2	70	1.11% ClO_2				
	quench				0.33% Na_2SO_3				
	E	10.0	60	70	2.18% NaOH	11.30	0	12.6	37.2
	D	3.3	2	70	1.11% ClO_2				
	quench				0.33% Na_2SO_3				
	E	10.0	60	70	2.18% NaOH	11.20	0	12.8	36.7

D_0^RE Lab Bleaching of Sweetgum Pulp, 0.10 KF

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Final pH	Residual %	Kappa No.	Bright. ISO
KF=0.10	Initial	IPST HW Sweet Gum, no carryover						15.6	
D (residual)	D	3.3	0.5	45	0.593% ClO_2	2.80	0.116		
D (residual)	D	3.3	0.5	45	0.593% ClO_2	2.85	0.114		
D (residual)	D	3.3	1	45	0.593% ClO_2	2.80	0.09		
D (residual)	D	3.3	1	45	0.593% ClO_2	2.85	0.094		
D (residual)	D	3.3	2	45	0.593% ClO_2	2.90	0.071		
D (residual)	D	3.3	2	45	0.593% ClO_2	2.85	0.072		
D quench E	D	3.3	0.5	45	0.593% ClO_2				
	quench				1.07% Na_2SO_3				
	E	10.0	60	70	1.36% NaOH	10.80		8.82	47.9
	D	3.3	0.5	45	0.593% ClO_2				
	quench				1.07% Na_2SO_3				
	E	10.0	60	70	1.36% NaOH	10.95		8.94	48.3
	D	3.3	1	45	0.593% ClO_2				
	quench				0.87% Na_2SO_3				
	E	10.0	60	70	1.36% NaOH	10.80		8.49	49.5
	D	3.3	1	45	0.593% ClO_2				
	quench				0.87% Na_2SO_3				
	E	10.0	60	70	1.36% NaOH	10.80		8.59	49.3
	D	3.3	2	45	0.593% ClO_2				
	quench				0.67% Na_2SO_3				
	E	10.0	60	70	1.36% NaOH	10.80		8.37	50.8
	D	3.3	2	45	0.593% ClO_2				
	quench				0.67% Na_2SO_3				
	E	10.0	60	70	1.36% NaOH	10.95		8.32	50.6

Appendix D - D_0^R(EPO) Trials on Lab Pulps

D_0^R(EPO) Trials of Pine Pulp, 0.15KF, Na_2SO_3 Quenching, No Carryover

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Final pH	Residual %	Kappa No.	Bright. ISO
KF=0.15	Initial	IPST Loblolly Pine - no carryover							29.1	
D (residual)	D	3.3	1	70	1.66% ClO_2		2.55	0.022		
D (residual)	D	3.3	1	70	1.66% ClO_2		2.55	0.022		
D (residual)	D	3.3	4	70	1.66% ClO_2		2.50	0.006		
D (residual)	D	3.3	4	70	1.66% ClO_2		2.50	0.006		
D quench	D	3.3	1	70	1.66% ClO_2		2.60			
(EPO)	Quench				0.22% Na_2SO_3					
	EPO*	10.0	60	80	2.84% NaOH	0.8% H_2O_2	11.05	0	6.63	54.4
	D	3.3	1	70	1.66% ClO_2		2.60			
	quench				0.22% Na_2SO_3					
	EPO*	10.0	60	80	2.84% NaOH	0.8% H_2O_2	11.00	0	6.51	56.2
	D	3.3	4	70	1.66% ClO_2		2.55			
	quench				0.05% Na_2SO_3					
	EPO*	10.0	60	80	2.84% NaOH	0.8% H_2O_2	11.05	0	6.46	55.5
	D	3.3	4	70	1.66% ClO_2		2.55			
	quench				0.05% Na_2SO_3					
	EPO*	10.0	60	80	2.84% NaOH	0.8% H_2O_2	11.05	0	6.07	58.0

D_0^R(EPO) Trials of Sweetgum Pulp, 0.15KF, Na_2SO_3 Quenching, No Carryover

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Final pH	Residual %	Kappa No.	Bright. ISO
KF=0.15	Initial	IPST HW Sweet Gum - no carryover							15.2	
D (residual)	D	3.3	1	70	0.869% ClO_2		2.85	0.048		
D (residual)	D	3.3	1	70	0.869% ClO2		2.80	0.049		
D (residual)	D	3.3	4	70	0.869% ClO2		2.80	0.005		
D (residual)	D	3.3	4	70	0.869% ClO_2		2.80	0.004		
D quench	D	3.3	1	70	0.869% ClO_2					
(EPO)	quench				0.45% Na_2SO_3					
	EPO*	10.0	60	80	2.26% NaOH	0.8% H_2O_2	11.10		6.19	69.2
	D	3.3	1	70	0.869% ClO_2					
	quench				0.45% Na_2SO_3					
	EPO*	10.0	60	80	2.26% NaOH	0.8% H_2O_2	11.05		6.09	69.6
	D	3.3	4	70	0.869% ClO_2					
	quench				0.04% Na_2SO_3					
	EPO*	10.0	60	80	2.26% NaOH	0.8% H_2O_2	10.80		6.0	70.9
	D	3.3	4	70	0.869% ClO_2					
	quench				0.04% Na_2SO_3					
	EPO*	10.0	60	80	2.26% NaOH	0.8% H_2O_2	11.30		5.87	72.2

D_0^R(EPO) Trials of Pine Pulp, 0.15KF, NaOH Quenching, With and Without Carryover

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Kappa No.	Bright. ISO
KF=0.15	Initial	IPST Loblolly Pine							29.1	
D quench (EPO)	D	3.3	1	70	1.66% ClO_2					
No carryover	quench				1.80%NaOH			7.3		
	EPO*	10.0	60	80	2.33% NaOH	0.8% H_2O_2			5.76	54.0
	D	3.3	1	70	1.66% ClO_2					
	quench				1.84% NaOH			7.5		
	EPO*	10.0	60	80	2.33% NaOH	0.8% H_2O_2		11.50	6.06	51.6
D quench (EPO)	D	3.3	1	70	1.66% ClO_2					
10% carryover	quench				1.84% NaOH			8.05		
	EPO*	10.0	60	80	2.33% NaOH	0.8% H_2O_2	10% D_0		6.42	50.6
	D	3.3	1	70	1.66% ClO_2					
	quench				1.84% NaOH			8.05		
	EPO*	10.0	60	80	2.33% NaOH	0.8% H_2O_2	10% D_0		6.39	49.6

*60-0 psig O_2 30 minutes

D_0^R(EPO) Trials of Sweetgum Pulp, 0.15KF, NaOH Quenching, With and Without Carryover

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Kappa No.	Bright. ISO
KF=0.15	Initial	IPST HW Sweet Gum							15.2	
D quench (EPO)	D	3.3	1	70	0.869% ClO_2					
No carryover	quench				NaOH			6.80		
	EPO*	10.0	60	80	2.33% NaOH	0.8% H_2O_2		11.35	5.84	67.3
	D	3.3	1	70	0.869% ClO_2					
	quench				NaOH			8.40		
	EPO*	10.0	60	80	2.33% NaOH	0.8% H_2O_2		11.50	5.81	70.2
D quench (EPO)	D	3.3	1	70	0.869% ClO_2					
10% carryover	quench				NaOH			7.60		
	EPO*	10.0	60	80	1.82% NaOH	0.8% H_2O_2	10% D_0	11.00	5.88	67.3
	D	3.3	1	70	0.869% ClO_2					
	quench				NaOH			7.75		
	EPO*	10.0	60	80	1.82% NaOH	0.8% H_2O_2	10% D_0	11.10	5.89	67.8

*60-0 psig O_2 30 minutes

Appendix E - D_0^R(EPO)(D/E/D) Bleaching Results

(D/E/D) Optimization for Loblolly Pine with 8 min. D_1

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s
KF=0.15	Initial	IPST Loblolly Pine								28.2			25
D quench (EPO)	D	3.3	1	60	1.58% ClO_2		0						
	quench				1.84% NaOH			8.50					
	EPO*	10.0	60	80	2.30% NaOH	0.8% H_2O_2	10% D_o	11.20	0.01				
	EPO*	10.0	60	80	2.30% NaOH	0.8% H_2O_2	10% D_o	11.10	0.01				
	D	3.3	1	70	1.66% ClO_2		0						
	quench				1.84% NaOH			8.50					
	EPO*	10.0	60	80	2.30% NaOH	0.8% H_2O_2	10% D_o	11.10	0.01				
	EPO*	10.0	60	80	2.30% NaOH	0.8% H_2O_2	10% D_o	11.10	0.01	6.02**	50.6**		16.8**
(D/E/D)	D		8	80	1.01% ClO_2		20% (EPO)	3.30	0.018		75.3	68.3	
	E		4	80	NaOH		100%	9.50					
	D	10.3	40	80	0.25% ClO_2		100%	3.90	0		80.2	76.5	16.2
	D	9.7	50	80	0.49% ClO_2		100%	3.60	0		82.2	78.6	16.0
	D	8.7	90	80	1.01% ClO_2		100%	3.40	0		85.4	81.9	14.9
	D		8	80	1.50% ClO_2		20% (EPO)	3.60	0.13		79.6	72.4	
	E		4	80	NaOH		100%	9.90					
	D	10.1	40	80	0.25% ClO_2		100%	4.00	0		83.6	79.8	14.8
	D	10.3	60	80	0.47% ClO_2		100%	3.90	0		84.9	81.5	13.8
	D	10.3	130	80	0.98% ClO_2		100%	3.40	0		87.0	83.9	14.1
	D		8	80	2.03% ClO_2		20% (EPO)	4.90	0.33		81.5	74.9	
	E		4	80	NaOH		100%	9.85					
	D	10.0	90	80	0.25% ClO_2		100%	4.10			86.3	83.3	11.4
	D	9.5	135	80	0.50% ClO_2		100%	4.00			86.5	83.7	11.2
	D	8.7	180	80	0.98% ClO_2		100%	3.90			87.7	85.1	11.5

*60-0 psig O_2 30 minutes ** combined (EPO) pulps

(D/E/D) Optimization for Sweetgum with 8 min. D_1

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s
KF=0.15	Initial	IPST HW Sweet Gum								15.2			29.2
D quench (EPO)	D	3.3	1	70	0.869% ClO_2								
	quench				1.195% NaOH			7.80					
	EPO*	10.0	60	80	1.89% NaOH	0.8% H_2O_2	10% D_o	11.10	0.004				
	EPO*	10.0	60	80	1.89% NaOH	0.8% H_2O_2	10% D_o	11.10	0.004	5.48	68.2		18.4
(D/E/D)	D		8	80	0.998% ClO_2		20% (EPO)	3.85	0.146		85.6	77.9	
	E		4	80	NaOH		100%	10.50					
	D	10.0	20	80	0.25% ClO_2		100%	4.00	0		89.0	84.0	
	D	9.8	25	80	0.52% ClO_2		100%	4.00	0		89.9	85.0	
	D	8.7	80	80	1.01% ClO_2		100%	4.00	0		90.4	85.9	16.3
	D		8	80	1.51% ClO_2		20% (EPO)	3.50	0.119		85.9	79.4	
	E		4	80	NaOH		100%	10.15					
	D	10.0	30	80	0.25% ClO_2		100%	4.00	0		89.4	85.4	
	D	9.4	35	80	0.49% ClO_2		100%	4.00	0		90.0	86.2	
	D	8.5	90	80	0.99% ClO_2		100%	4.00	0		91.0	87.3	
	D		8	80	2.00% ClO_2		20% (EPO)	4.60	0.223		86.3	78.6	
	E		4	80	NaOH		100%	10.20					
	D	10.0	35	80	0.25% ClO_2		100%	4.20	0		89.9	85.4	
	D	9.8	50	80	0.50% ClO_2		100%	4.10	0		90.6	85.8	
	D	8.7	95	80	0.98% ClO_2		100%	4.85	0		90.4	86.6	

*60-0 psig O_2 30 minutes ** combined (EPO) pulps

(D/E/D) Optimization for Sweetgum with 60 min., 80°C D_1

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s
KF=0.15	Initial	IPST HW Sweet Gum								15.2			29.2
D quench (EPO)	D	3.3	1	65	0.861% ClO_2								
	quench				1.21% NaOH			7.90					
	EPO*	10.0	60	80	1.87% NaOH	0.8% H_2O_2	10% D_o	10.70	0				
	EPO*	10.0	60	80	1.87% NaOH	0.8% H_2O_2	10% D_o	11.05	0	5.39	67.1		16
(D/E/D)	D		60	80	1.011% ClO_2		20% (EPO)	3.60	0		82.5		
	E		4	80	NaOH		100%	10.80					
	D	10.0	25	80	0.25% ClO_2		100%	4.20	0		87.9	83.4	14.4
	D	9.7	35	80	0.50% ClO_2		100%	4.00	0		88.5	83.9	14.5
	D	8.7	70	80	1.02% ClO_2		100%	4.00	0		88.6	84.1	14.0
	D		60	80	1.52% ClO_2		20% (EPO)	3.80	0		84.5	79.2	
	E		4	80	NaOH		100%	10.90					
	D	10.0	30	80	0.25% ClO_2		100%	4.10	0		89.1	85.4	10.2
	D	9.6	35	80	0.50% ClO_2		100%	4.10	0		89.7	86.0	10.2
	D	8.7	75	80	0.993% ClO_2		100%	4.00	0		89.0	87.0	10.8
	D		60	80	2.04% ClO_2		20% (EPO)	4.30	0		87.6		
	E		4	80	NaOH		100%	10.80					
	D	9.8	30	80	0.25% ClO_2		100%	4.20	0		89.7	85.8	8.4
	D	9.8	50	80	0.514% ClO_2		100%	4.20	0		90.6	87.0	8.3
	D	8.7	100	80	0.996% ClO_2		100%	4.30	0		91.3	88.0	8.2

*60-0 psig O_2 30 minutes ** combined (EPO) pulps

(D/E/D) Optimization for Loblolly Pine with 60 min., 70°C D_1

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s
KF=0.15	Initial	IPST Loblolly Pine (SW)								25.8			26.7
D quench	D_o	3.3	1	65	1.52% ClO_2								
(EPO)	quench				1.84% NaOH			8.70					
	(EPO)	10	60	80	2.33% NaOH	0.80% H_2O_2	10% D_0	11.10	trace	4.8	51.2		13.9
(D/E/D)	D_1	10	60	70	1.00% ClO_2		20% (EPO)	4.10	trace		80.8	73.7	
	E	10	4	80	0.90% NaOH		100% D_1	10.40	trace				
	D_2	10			0.25% ClO_2		100% E	4.05	trace		84.9	80.7	13.4
	D_2	9.5			0.50% ClO_2		100% E	4.00	trace		86.3	82.3	13.4
	D_2	8.5			1.02% ClO_2		100% E	3.90	trace		88.4	85.0	13.1

D^R(EPO)(D/E/D) Pine Pulp for Testing with 8 min., 80°C D_1

	Stage	Cons. %	Temp. °C	Time min.	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s	AOX kg/ADMT
KF=0.15	Initial	IPST Loblolly Pine (SW)								28.2			25.0	
D quench	D_o	3.3	70	1	1.62% ClO_2									
(EPO)	quench				1.84% NaOH			8.50						
	(EPO)	10	80	60	2.33% NaOH	0.80% H_2O_2	10% D_0	11.30	trace	6.1	47.5		19.9	
(D/E/D)	D_1	10	**80**	**8**	1.46% ClO_2		20% (EPO)	4.30	trace		77.4	74.2		
	E	10	80	4	0.75% NaOH		100% D_1	10.35	trace					combined
	D_2	9.0	80	90	0.79% ClO_2		100% E	4.00	trace		86.6	83.0	15.8	0.66

D^R(EPO)(D/E/D) Pine Pulp for Testing with 60 min., 70°C D_1

	Stage	Cons. %	Temp. °C	Time min.	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s	AOX kg/ADMT
KF=0.15	Initial	IPST Loblolly Pine (SW)								25.8			26.7	
D quench	D_o	3.3	70	1	1.51% ClO_2									D_o^r (EPO)
(EPO)	quench				1.81% NaOH			8.15						0.33
	(EPO)	10	80	60	2.67% NaOH	0.80% H_2O_2	10% D_0	11.20	trace	4.8	52.4		13.3	(D/E/D)
(D/E/D)	D_1	10	**70**	**60**	0.97% ClO_2		20% (EPO)	4.50	trace		82.0	74.9		0.16
	E	10	80	4	0.80% NaOH		100% D_1	10.60	trace					combined
	D_2	10.2	80	35	0.27% ClO_2		100% E	4.00	trace		85.5	81.4	12.4	0.50

D^R(EPO)(D/E/D) Sweetgum Pulp for Testing with 8 min., 80°C D_1

	Stage	Cons. %	Temp. °C	Time min.	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s	AOX kg/ADMT
KF=0.15	Initial	IPST Sweetgum (HW)								15.2			29.2	
D quench	D_o	3.3	70	1	0.85% ClO_2									
(EPO)	quench				1.20% NaOH			7.90						
	(EPO)	10	80	60	1.96% NaOH	0.80% H_2O_2	10% D_0	11.40	trace	5.9	66.6		17.4	
(D/E/D)	D_1	10	**80**	**8**	0.99% ClO_2		20% (EPO)	3.85	trace		82.5	74.3		
	E	10	80	4	0.85% NaOH		100% D_1	9.80	trace					combined
	D_2	10	80	25	0.29% ClO_2		100% E	4.20	trace		87.5	82.6	16.7	0.35

D^R(EPO)(D/E/D) Sweetgum Pulp for Testing with 60 min., 70°C D_1

	Stage	Cons. %	Temp. °C	Time min.	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s	AOX kg/ADMT
KF=0.15	Initial	IPST Sweetgum (HW)								15.2			29.2	
D quench	D_o	3.3	70	1	0.85% ClO_2									D_o^r (EPO)
(EPO)	quench				1.21% NaOH			8.00						0.33
	(EPO)	10	80	60	2.16% NaOH	0.80% H_2O_2	10% D_0	11.20	trace	5.7	65.9		16.5	(D/E/D)
(D/E/D)	D_1	10	**70**	**60**	1.00% ClO_2		20% (EPO)	3.95	trace		85.5	79.5		0.09
	E	10	80	4	0.80% NaOH		100% D_1	10.40	trace					combined
	D_2	9.8	80	30	0.35% ClO_2		100% E	4.20	trace		88.8	85.0	15.8	0.38

Appendix F - D(EPO)D Sequence Results

D(EPO)D Optimization of Loblolly Pine

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s
KF=0.15	Initial	IPST Loblolly Pine								28.2			25
D(EPO)D	D	3.3	30	60	1.59% ClO_2		0	2.35					
SW Control	EPO*	10.0	60	80	4.11% NaOH	0.8% H_2O_2	10% D_o	11.50	0				
	EPO*	10.0	60	80	3.78% NaOH	0.8% H_2O_2	10% D_o	11.10	0	5.3	57.9		18.3
	D	10.0	20	80	0.30% ClO_2		20% EPO	4.20	0		66.6	60.8	15.8
	D	10.0	60	80	0.592% ClO_2		20% EPO	3.90	0		70.4	65.3	15.9
	D	10.0	95	80	1.185% ClO_2		20% EPO	4.30	0		81.0	75.0	16.4
	D	10.0	180	80	2.525% ClO_2		20% EPO	3.10	0		86.1	81.4	15.9

D(EPO)D Optimization of Sweetgum

	Stage	Cons. %	Time min.	Temp. °C	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s
KF=0.15	Initial	IPST HW Sweet Gum								15.2			29.2
D(EPO)D	D	3.3	30	60	0.845% ClO_2		0	2.80					
HW Control	EPO*	10.0	60	80	3.22% NaOH	0.8% H_2O_2	10% D_o	11.40	0				
	EPO*	10.0	60	80	3.22% NaOH	0.8% H_2O_2	10% D_o	11.40	0	5.3	71.9		15.2
	D	10.0	20	80	0.30% ClO_2		20% EPO	4.30	0		80.9	73.7	12.7
	D	10.0	60	80	0.592% ClO_2		20% EPO	3.90	0		83.8	77.2	12.4
	D	10.0	95	80	1.20% ClO_2		20% EPO	3.90	0		85.3	80.1	12.6
	D	10.0	180	80	2.44% ClO_2		20% EPO	4.20	0		89.2	84.4	8.7

D(EPO)D Pine Pulp for Testing

	Stage	Cons. %	Temp. °C	Time Min.	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s	AOX kg/ADMT
KF=0.15	Initial	IPST Loblolly Pine (SW)								25.8			26.7	
D(EPO)D	D_o	3.3	70	30	1.53% ClO_2			2.20	0					
SW Control	(EPO)	10	80	60	4.00% NaOH	0.80% H_2O_2	10% D_o	11.20	trace	4.4	55.3		13.2	combined
	D_1	9.7	**80**	120	2.35% ClO_2		20% EPO	3.50	trace		85.3	80.4	11.2	0.62

D(EPO)D Sweetgum Pulp for Testing

	Stage	Cons. %	Temp. °C	Time Min.	Chemical %	Chemical %	Carryover	Final pH	Residual %	Kappa No.	Bright. ISO	Reverted Bright.	Viscosity mPa.s	AOX kg/ADMT
KF=0.15	Initial	IPST Sweetgum (HW)								15.2			29.2	
D(EPO)D	D_o	3.3	70	30	0.86% ClO_2			2.80	0					
SW Control	(EPO)	10	80	60	3.11% NaOH	0.80% H_2O_2	10% D_o	11.35	trace	4.9	69.6		14.4	combined
	D_1	9.4	**80**	95	2.45% ClO_2		20% EPO	4.25	trace		89.0	83.0	9.6	0.55

Appendix G – Strength Results

$D^R(EPO)(D/E/D)$ – Pine D_1 – 1.5% ClO_2 8 min., 80°C D_2 0.80% ClO_2

PFI Revolutions	0	1000	2000	3000
Freeness (mls)		658	516	371
Basis Weight (g/m^2)		63.90	65.44	66.37
Caliper (mm)		101.5	105.2	102.0
Standard Deviation		1.50	1.80	2.90
Density (g/cm^3)		0.629	0.622	0.651
Burst Index ($kPa.m^2/g$)		4.82	5.94	6.70
Standard Deviation		0.378	0.390	0.447
Tear Index ($mN.m^2/g$)		19.11	15.53	13.09
Standard Deviation		0.440	0.350	0.943
Tensile Index (N.m/g)		62.14	72.29	73.54
Standard Deviation		0.798	2.06	3.16
TEA Index (mJ/g)		1497	1847	1983
Standard Deviation		134.1	69.6	182.8
Specific Modulus (N.m/g)		5780	5965	6022
Standard Deviation		268	763	330
Stretch (%)		3.44	3.76	4.02
Standard Deviation		0.231	0.135	0.233
ZST Index (N.m/g)		130.4	139.7	130.8
Standard Deviation		4.45	7.60	8.03
Dirt (mm^2/m^2)	7.12			

$D^R(EPO)(D/E/D)$ – Pine D_1 – 1.0% ClO_2 60 min., 70°C D_2 0.30% ClO_2

PFI Revolutions	0	1000	1700	2400	3100	3800
Freeness (mls)		670	571	442	324	223
Basis Weight (g/m^2)		67.06	65.22	66.46	66.16	64.99
Caliper (mm)		118.1	103.7	107.4	104.3	96.8
Standard Deviation		2.65	1.80	1.41	2.21	1.81
Density (g/cm^3)		0.568	0.629	0.619	0.634	0.672
Burst Index ($kPa.m^2/g$)		4.67	5.60	6.16	6.28	6.89
Standard Deviation		0.232	0.343	0.252	0.330	0.346
Tear Index ($mN.m^2/g$)		17.76	13.82	12.61	11.77	10.25
Standard Deviation		1.09	0.553	0.526	0.269	0.204
Tensile Index (N.m/g)		56.80	66.87	74.39	77.31	77.74
Standard Deviation		1.16	2.49	4.30	6.64	6.53
TEA Index (mJ/g)		1373	1585	1799	1712	1918
Standard Deviation		95.3	146	195	287	378
Specific Modulus (N.m/g)		5733	5893	6659	6408	7080
Standard Deviation		464.7	763.7	712.9	457.1	794.8
Stretch (%)		3.41	3.52	3.59	3.37	3.70
Standard Deviation		0.174	0.279	0.269	0.329	0.546
ZST Index (N.m/g)		109.1	116.3	112.9	114.1	124.3
Standard Deviation		6.69	8.82	9.32	7.02	7.71
Dirt (mm^2/m^2)	6.90					

$D^R(EPO)(D/E/D)$ – Sweetgum D_1 – 1.0% ClO_2 8 min., 80°C D_2 0.30% ClO_2

PFI Revolutions	0	1250	3000
Freeness (mls)	700	550	326
Basis Weight (g/m^2)	67.96	65.40	65.61
Caliper (□m)	136.3	109.5	103.5
Standard Deviation	2.70	1.60	2.70
Density (g/cm^3)	0.499	0.597	0.634
Burst Index ($kPa.m^2/g$)	0.808	2.81	4.08
Standard Deviation	0.061	0.158	0.210
Tear Index ($mN.m^2/g$)	6.59	10.74	10.21
Standard Deviation	0.372	0.602	0.088
Tensile Index (N.m/g)	18.89	48.21	56.50
Standard Deviation	0.530	2.65	3.70
TEA Index (mJ/g)	132.6	977.0	1188
Standard Deviation	12.6	144	218
Specific Modulus (N.m/g)	3780	5637	6070
Standard Deviation	192	164	98.0
Stretch (%)	1.03	2.78	2.99
Standard Deviation	0.083	0.237	0.348
ZST Index (N.m/g)	118.2	125.7	133.3
Standard Deviation	3.20	7.56	9.59

$D^R(EPO)(D/E/D)$ – Sweetgum D_1 – 1.0% ClO_2 60 min., 70°C D_2 0.35% ClO_2

PFI Revolutions	0	500	1250	2000	2750	3500
Freeness (mls)		657	545	463	366	230
Basis Weight (g/m^2)		65.47	65.78	65.47	65.85	66.18
Caliper (mm)		125.6	120.6	118.6	106.5	116.6
Standard Deviation		4.58	3.44	3.08	3.33	1.86
Density (g/cm^3)		0.521	0.546	0.552	0.618	0.568
Burst Index ($kPa.m^2/g$)		1.87	2.80	3.24	3.85	4.15
Standard Deviation		0.045	0.136	0.194	0.201	0.199
Tear Index ($mN.m^2/g$)		8.54	10.23	10.41	10.13	10.35
Standard Deviation		0.301	0.473	0.112	0.291	0.186
Tensile Index (N.m/g)		32.69	44.96	48.87	58.39	57.15
Standard Deviation		1.29	2.15	1.03	2.22	1.82
TEA Index (mJ/g)		472.1	851.7	1157	1357	1448
Standard Deviation		63.8	148	85.7	168	164
Specific Modulus (N.m/g)		5016	5647	5656	6361	5710
Standard Deviation		153.1	457.4	136.7	322.9	436.7
Stretch (%)		1.97	2.59	3.22	3.25	3.58
Standard Deviation		0.197	0.324	0.151	0.376	0.346
ZST Index (N.m/g)		104.5	112.3	106.6	118.7	116.1
Standard Deviation		4.51	9.43	7.29	8.70	7.14
Dirt (mm^2/m^2)	7.70					

D(EPO)D Pine Pulp D_1 2.4% ClO_2

PFI Revolutions	0	1000	1700	2400	3100	3800
Freeness (mls)		654	539	423	300	231
Basis Weight (g/m^2)		64.57	66.47	64.90	64.92	65.69
Caliper (mm)		110.0	110.5	105.8	102.8	102.1
Standard Deviation		3.80	2.05	1.63	2.93	0.81
Density (g/cm^3)		0.587	0.602	0.611	0.632	0.644
Burst Index ($kPa.m^2/g$)		4.70	5.49	5.97	6.32	6.68
Standard Deviation		0.249	0.212	0.253	0.365	0.547
Tear Index ($mN.m^2/g$)		18.04	13.69	12.57	12.12	12.33
Standard Deviation		0.190	0.282	0.456	0.398	0.325
Tensile Index (N.m/g)		56.30	65.02	68.54	68.45	76.90
Standard Deviation		3.73	5.12	4.89	7.99	5.05
TEA Index (mJ/g)		1261	1446	1438	1453	1999
Standard Deviation		222.9	215.9	140.7	228.2	308.3
Specific Modulus (N.m/g)		5712	6102	6496	6818	6191
Standard Deviation		109.9	281.2	287.6	260.2	790.9
Stretch (%)		3.18	3.30	3.15	3.05	3.95
Standard Deviation		0.332	0.204	0.140	0.259	0.497
ZST Index (N.m/g)		113.0	109.5	120.1	120.4	118.2
Standard Deviation		9.29	4.33	10.25	9.51	6.43
Dirt (mm^2/m^2)	6.79					

D(EPO)D Sweetgum Pulp D_1 2.4% ClO_2

PFI Revolutions	0	500	1250	2000	2750	3500
Freeness (mls)		621	529	455	362	232
Basis Weight (g/m^2)		64.50	65.16	64.72	65.08	64.88
Caliper (mm)		118.5	129.7	117.9	117.9	113.2
Standard Deviation		1.43	4.20	3.64	2.75	2.31
Density (g/cm^3)		0.544	0.502	0.549	0.552	0.573
Burst Index ($kPa.m^2/g$)		1.73	2.38	3.12	3.54	4.12
Standard Deviation		0.077	0.151	0.128	0.204	0.200
Tear Index ($mN.m^2/g$)		8.09	8.86	8.75	8.89	8.46
Standard Deviation		0.848	0.365	0.220	0.261	0.172
Tensile Index (N.m/g)		33.09	39.27	44.15	51.76	56.23
Standard Deviation		0.777	1.06	3.78	2.34	1.04
TEA Index (mJ/g)		421.6	703.5	856.4	1207	1309
Standard Deviation		59.4	45.6	264	151	79.1
Specific Modulus (N.m/g)		5411	5543	5747	6161	6449
Standard Deviation		199.5	171.1	253.8	194.3	158.8
Stretch (%)		1.80	2.40	2.60	3.18	3.19
Standard Deviation		0.173	0.142	0.568	0.278	0.166
ZST Index (N.m/g)		95.0	98.5	97.5	100.4	102.2
Standard Deviation		2.80	7.09	6.74	7.63	6.10
Dirt (mm^2/m^2)	6.79					